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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

341. **Means for collecting and keeping gaseous samples.** M. A. Guatelli (School of Pharm. & Biochem., Faculty of Medical Sciences, Buenos Aires). *Act. Bioquim., Santa Fé*, 1956, **5** (1), 6–13.—A general discussion covers descriptions of ampoules or vacuum bulbs; vacuum flasks; ampoules for displacement with gases or liquids; ampoules for displacement with gases or liquids for gaseous samples of variable composition; metallic collectors; ordinary glass flasks; absorbers, bubblers, etc.; and other devices. A bibliography of 10 books is listed.
D. LEIGHTON

342. **Analytical reactions of some amidoximes. VII. Malonamic amidoxime.** M. Kuraš and R. Ružička (Chem. Inst., Olomouc, Czechoslovakia). *Chem. Listy*, 1955, **49** (12), 1897–1898.—The preparation of malonamic amidoxime (**I**) and its reactions with some metal ions are described. The basic salts of **I** with Ag^+, Hg^{2+}, Pb^{2+} and Ni^{2+} were isolated and their constitution determined.
J. ZÝKA

343. **Spot reactions for examination of filter-papers.** F. Feigl (Min. Agric., Rio de Janeiro, Brazil). *Z. anal. Chem.*, 1956, **152** (1–3), 52–55.—Specific spot-tests which permit differentiation between "quantitative" (ash-free) papers (*A*) and "qualitative" papers (*B*) of different origin are described. With Nessler reagent, *A* give a strongly positive reaction for NH_4^+, while *B* give a negative or but weakly positive reaction. With 3% 2:2′-dipyridyl in 40% thioglycollic acid or with *o*-phenanthroline, *B* give a bright-red spot (test for Fe) within 2 min., whereas *A* give no reaction. Moreover with the dye "Blue ciel au chrome" (CIBA), *B* give a bright-blue colour (test for Ca and Mg) in the presence of NH_3 vapour, whilst *A* give no colour. Such spot tests on the papers themselves without prior ashing save time and are of use in the control of 'demineralisation.'
J. P. STERN

344. **A new analytical principle: hindrance of extraction.** Z. G. Szabo, M. T. Beck and K. Toth (Inst. Inorg. and Anal. Chem., Univ. Szeged, Hungary). *Naturwissenschaften*, 1956, **43** (7), 156 (in English).—The sensitivity of methods for the determination of anions based on their fading effect on a coloured complex, *e.g.*, the effect of F^- on the Fe^{3+} - SCN^- system, may be increased if the change of absorbancy in the organic phase is examined after shaking with a proper solvent, *i.e.*, the hindrance of extraction of the anion is determined. The smallest amount of F^- that can be determined by the above method can be reduced from 30 μg to 10 μg in 50 ml by the use of *n*-pentanol.
E. KAWERAU

345. **Thermal stability of analytical standards. III.** C. Duval, C. Wadier and Y. Servigne (Lab. Recherches Micro-analytiques, 11 rue Pierre Curie, Paris). *Anal. Chim. Acta*, 1956, **15** (3), 223–225.—Thermogravimetric curves and i.r. absorption spectra are reported for $KMnO_4$, $Ce(SO_4)_2.3H_2O$, KI, KIO_3, $KBrO_3$, $Na_2C_2O_4$, $Na_4P_2O_7.10H_2O$, $Al_2(SO_4)_3.16H_2O$, D-tartaric acid, sodium citrate hydrate, Na_2O_2 and ammonium molybdate. The ammonium molybdate had the composition $7MoO_3.3(NH_4)_2O.4H_2O$ and was stable up to 109°. The information given enables the max. temp. of drying to be fixed, as well as the rapid identification of the compounds or of their possible impurities (*cf. Anal. Abstr.*, 1955, **2**, 3272; 1956, **3**, 1229).
W. J. BAKER

346. **Brazilin as acid - base indicator.** J. Bitskei and P. Móritz (Tech. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 250–251.—The 1% ethanolic soln. of brazilin (**I**) that was used was stable for a long time. The colour-change interval is pH 5·85 to 7·73, and the sharp change is from greenish yellow to reddish violet. There are also other, less definite colour changes at various pH values; thus **I** may also be suitable for pH determinations. The use of **I** for the titration of strong acids and of strong bases is described.
A. G. PETO

347. **Standardisation of 0·1 *N* potassium methoxide with 2-phenyl-4-quinolinecarboxylic acid [cinchophen].** I. Gyenes (Pharm. Factory of Kőbánya, Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 237–239.—The use of cinchophen instead of benzoic acid for the standardisation of 0·1 *N* K methoxide gives a sharper end-point and there is no formation of a ppt. in an anhydrous medium. The determination of cinchophen, *p*-hydroxypropiophenone, 8-hydroxyquinoline and stilboestrol was carried out in acetone, acetone - pyridine (4:1), benzene - pyridine (2:1) and acetone - pyridine - methanol (70:30:2) soln., with thymol blue and azo violet as indicators; the results were similar.
N. E.

348. **Zinc complex of Eriochrome blue black R ("Zinchrome R") as stable indicator for EDTA titrations.** K. L. Cheng (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Chemist Analyst*, 1956, **45** (3), 79–81.—Zinchrome R, the zinc complex of 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid, is recommended for the EDTA titration of water hardness in place of Eriochrome black T owing to its greater stability in solution. It may also be used for EDTA titrations of Ca, Mg, Zn, Cd and Pb.
C. A. SLATER

349. **Analysis for industry. [Indicators for EDTA titrations.]** T. S. West. *Ind. Chem. Mfr*, 1956, **32**, 128–129.—A survey is given of the literature relating to the use of the following indicators in titrations with EDTA—(*i*) 3:3′-dimethylnaphthidine (redox indicator, Zn); (*ii*) 1-(2-pyridylazo)-2-naphthol (Cu, also Ni, Co, Cd, Pb, Fe, Zn, In); (*iii*) alizarin S (Bi, Al, Th); (*iv*) catechol and

salicylic acid (Fe^{III}); (*v*) Alizarol Cyanone RC, Eriochrome cyanine RC (Zr); (*vi*) thiourea, dithizone (Al), morin (Ga and In); and (*vii*) screened complexiметric indicators, including murexide and Eriochrome black T. (24 references.)
S.C.I. ABSTR.

350. **The use of Metanil yellow, Astral blue, Xylene blue and Setoglaucin as indicators in cerimetry.** J. Bognár and Z. Nádler (Rákosi Mátyás Polytech. Univ. Heavy Industries, Miskolc, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 51–60 (in German).—This paper has been published in Hungarian in *Magyar Kém. Foly.*, 1955, **61** (11), 372; *cf. Anal. Abstr.*, 1956, **3**, 2385.
A. R. ROGERS

351. **Induced reactions in dichrometry [dichromate titrations] with hydroquinone [quinol] as inductor.** G. Gopala Rao and T. P. Sastri (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **152** (4), 270–275 (in English).—Oxalic acid, glycerol (**I**), lactic acid (**II**), glucose, citric acid and malic acid interfere in the determination of quinol by $K_2Cr_2O_7$. Normally these substances react slowly with $K_2Cr_2O_7$, but quinol induces a more rapid reaction. The interfering substances are listed above in order of decreasing ease of oxidation. An additional source of error with **I** and **II** is due to interference with the production of the colour change of diphenylbenzidine indicator; this colour change is completely suppressed by tartaric acid. J. P. STERN

352. **Visual titrations with diethyldithiocarbamate. VII. Standardisation of diethyldithiocarbamate solutions with silver nitrate.** R. Wickbold (Chem. Werke Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **153** (1), 24–27.—The direct titration procedure with diethyldithiocarbamate and dithizone indicator described for Pb (*cf. Anal. Abstr.*, 1957, **4**, 446) gives an accurate method for determining Ag in amounts down to 0·1 mg. Moreover, $AgNO_3$ can be used for the standardisation of the only slightly stable diethyldithiocarbamate soln. *Procedure*—A suitable vol. of standard $AgNO_3$ soln. is weighed out in a weighing pipette. Acetic acid - Na acetate buffer soln. (pH 5) (10 ml) is added and the soln. is diluted to 100 ml. After adding 5 ml of dithizone indicator (5 mg per litre of $CHCl_3$) and 10 ml of $CHCl_3$, the soln. of Ag is titrated with the diethyldithiocarbamate soln. The indicator becomes red and later changes to yellow; at the equiv. pt. it turns sharply to green. For $\simeq$ 0·001 *N* soln., only 2 ml of indicator is used. J. H. WATON

353. **Selection of solvent proportions for paper chromatography. Ethyl acetate - acetic acid - water system.** D. F. Durso and W. A. Mueller (Buckeye Cellulose Corp., Memphis, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1366–1368.—Variation of the composition of this solvent system has been related, by statistical methods, to the rate and degree of separation of monosaccharides. Reference to the data obtained enables a suitable selection to be made of solvent proportions for the efficient separation of a particular mixture. G. P. COOK

354. **Some theoretical and experimental considerations of pH gradient elution analysis.** K. A. Piez (Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1451–1454.—General equations relating pH changes to eluate volume are derived and the selection of optimum conditions for any desired gradient is discussed, with the aid of six graphs. The addition to one buffer of another buffer or of an acid or base, under a variety of experimental conditions, is considered. E. G. CUMMINS

355. **A consideration of factors governing the separation of substances by gas - liquid partition chromatography.** D. W. Grant and G. A. Vaughan (Coal Tar Research Ass., Oxford Rd., Gomersal, nr. Leeds). *J. Appl. Chem.*, 1956, **6** (4), 145–153.—The retention volumes (V_R) of two substances *A* and *B* in a gas - liquid chromatogram are theoretically related by the equation, $\log_{10}$ (V_R for *A*)/(V_R for *B*) = $Kd/2{\cdot}303\,\boldsymbol{RT} - \log_{10}M_A/M_B$, where *K* is the Trouton constant, *d* is the difference in b.p. and *M* is the mol. wt. The calculated ratio of retention vol. for a number of substances on different stationary phases is compared with the experimental values, with fair agreement. From this equation also, $\log_{10}$ retention vol. ratio should be proportional to $1/T$, which is also found in practice. The equation fails for compounds of dissimilar type. It is also shown theoretically that the number of theoretical plates in a column, *r*, is $t^2r^2T^2/K^2d^2$, where *t* is the number of standard deviations by which the maxima must be separated. As a consequence, a max. column operating temp. for separation by three standard deviations is given for aromatic hydrocarbons by $T_{max.} = dr\frac{1}{2}/0{\cdot}08$. The equation is tested for a number of compounds and produces good agreement. The factors affecting column efficiency are discussed and it is pointed out that particle size of Celite kieselguhr does not have much effect since the large particles are aggregates of the same small diatomaceous particles. The effect of increasing the ratio of stationary phase to Celite is also investigated. E. J. H. BIRCH

356. **Use of ion exchangers in analytical chemistry. VIII. Summary of general working principles.** D. Jentzsch (Gartenstr. 48, Altena, Westphalia, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 134–146.—Experimental conditions, results and applications of quant. separations of ions in HCl soln. with a basic anion exchanger are summarised (*cf. Ibid.*, 1956, **150**, 241, and earlier papers). Differences in the plots relating elution const. to acid concn. are discussed and their applicability to the separation of ions of metal chloro-complexes without the need for prior empirical experimentation is stressed.
J. P. STERN

357. **Studies on polarographic analysis. XVIII. Use of a double complexing agent as supporting electrolyte. (2) The EDTA - KCN base solution.** Masayoshi Ishibashi, Taitiro Fujinaga and Masanori Sato (Faculty of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 696–701.—The polarographic waves of various metal ions (especially of Bi) were studied in a supporting electrolyte containing 0·1 *M* EDTA (disodium salt) and 0·1 *M* KCN (pH 9·7) and the result applied to the determination of a small amount of Bi (10^{-5} to 10^{-7} *M*) in the presence of Cu ($< 10^{-2}$ *M*). The sample soln. is neutralised to methyl red and successively treated with KCN, EDTA and ethanol to produce the above-mentioned soln. in 10% ethanol. The $E_{\frac{1}{2}}$ of the Bi wave is $-$ 0·85 V *vs.* the S.C.E., the height being proportional to its concn., whilst Cu fails to give a reduction wave. K. SAITO

358. **The characterisation of aerosols.** L. le Bouffant ("Cerchar," Lab. de Verneuil, Oise, France). *Chim. Anal.*, 1956, **38** (9), 303–313.—The various methods for the sampling and characterisation of aerosols are reviewed. (19 references.)
C. A. SLATER

2.—INORGANIC ANALYSIS

359. **A colour reagent for cations.** D. Harrop and E. F. G. Herington (Chemical Research Lab., Teddington, Middx., England). *Analyst*, 1956, **81**, 499–500.—A reagent is described for the detection of cations in paper chromatography. Trisodium pentacyanoamminoferrate is prepared by the reaction of NH_3 with sodium nitroprusside (Herington, *Brit. Abstr. C*, 1953, **309**). The reagent is prepared by dissolving 0·7 g of this compound in 20 ml of water and pouring the soln. into a soln. of 0·25 g of rubeanic acid in 10 ml of ethanol. At room temp. it is stable only for the day of preparation, but may be stored at − 15° for at least a month. The chromatographic paper is sprayed with the reagent and then washed with acetic acid ($\simeq$ 0·2 *N*). The colours shown by various cations are tabulated and the relative sensitivities of the tests are indicated. Some of the differences shown by metals in the same periodic group, *e.g.*, Zn (red), Cd (blue), and by the same metal in different valency states, *e.g.*, Hg^+ (brown), Hg^{2+} (green), are remarkable. A. O. JONES

360. **Visual titrations with diethyldithiocarbamate. I. General.** R. Wickbold (Chem.-Werke Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **152** (4), 259–262.—The properties of Na diethyldithiocarbamate (**I**) of value in the determination of heavy-metal ions are discussed. The low solubility in water, good solubility in organic solvents, and colour of the complexes are particularly valuable. The water solubility of the complexes increases in the following order—Hg, Ag, Cu, Ni, Co, Pb, Bi, Cd, Tl^{III}, Sb^{III}, Zn, Mn^{II}, Fe^{III}. Earlier members of the series displace later members from their complexes with **I**; this is best accomplished by shaking the chloroform soln. of the complex with an aq. soln. of the free metal ion at pH 5. This provides the basis for the titrimetry of heavy-metal ions, except for Ni and Co, the complexes of which do not react in acid soln. with ions of Cu or Hg. J. P. STERN

361. **EDTA titrations using copper - PAN complex as indicator.** H. Flaschka and H. Abdine (Nat. Res. Council, Dokki-Cairo, Egypt). *Chemist Analyst*, 1956, **45** (3), 58–61.—A sensitive method for the estimation of Zn, Cd, Hg, Ni, Co, Ga, In and V is described. The method depends on the use of the indicator 1-(2-pyridylazo)-2-naphthol (PAN) which was introduced by Cheng and Bray (*Anal. Chem.*, 1955, **27**, 782). The general procedure is as follows. The sample soln. is neutralised, and saturated Na acetate soln. (a few drops) is added, followed by acetic acid [50% (w/w)] to give the appropriate pH (for Zn and Cd, 4·5; for Pb and Ga, 3 to 3·5). To this soln. are added a copper - EDTA soln. [2 to 3 drops of a soln. containing EDTA (37·22 g per litre of disodium salt) and one equiv. of $CuSO_4$] and enough PAN indicator soln. (0·1% soln. in ethanol) to give an intense violet colour. The soln. is heated to boiling point and titrated against standard EDTA soln. until the colour changes to clear yellow. C. A. SLATER

362. **Bromine - mercuric sulphate oxidising system in quantitative mineral analysis.** J. Modiano and J.-C. Pariaud. *Compt. Rend.*, 1955, **241**, 500.—The introduction of $HgSO_4$ into a *N* solution of Br in H_2SO_4, used for various org. determinations (*Ibid.*, 1953, **236**, 1897), has now been applied to the oxidation of Fe^{II}, Sn^{II}, As^{III}, Sb^{III}, $S_2O_3^{2-}$ and NO_2^-. Potentiometric and back-titration methods are both convenient; the latter method takes < 10 min. The determination is carried out in a stoppered Erlenmeyer flask, partially evacuated through a side-arm fitted with a stopcock, into which is introduced 10 ml of 0·1 *N* KBr - $KBrO_3$ solution, 5 ml of 6 *N* H_2SO_4, and, after 1 min., $\simeq$ 10 ml of 0·2 *N* $HgSO_4$. The sample is then added, followed by 10 ml of 3 *N* NaCl, liberating excess of Br from the complex; 20 ml of KI (20%) solution is then added and the mixture is immediately titrated with 0·05 *N* $Na_2S_2O_3$. S.C.I. ABSTR.

363. **Volumetric studies in oxidation - reduction reactions. IX. Reduction with ferrous ethylenediamine sulphate. Sodium metavanadate method.** B. Singh and S. Singh (Punjab Univ. Coll., Hoshiarpur, India). *Anal. Chim. Acta*, 1956, **15** (3), 277–278.—Ferrous ethylenediamine sulphate (**I**) can be used as a reducing agent in acid medium for the indirect volumetric determination of $KBrO_3$, KIO_4, $K_2Cr_2O_7$, $K_3Fe(CN)_6$, $KMnO_4$, $K_2S_2O_8$, H_2O_2, $Ce(SO_4)_2$ and $NaVO_3$. An excess of a 0·05 *N* soln. of **I** is added to the sample in the presence of a mixture of dil. H_2SO_4 and H_3PO_4, and the unused **I** is then titrated with 0·05 *N* sodium metavanadate soln., with diphenylbenzidine as indicator. A slight modification is necessary for samples containing $K_3Fe(CN)_6$. The method is valid for concn. of 0·35 to 0·95 milli-equiv. of each compound. W. J. BAKER

364. **Precipitation paper-chromatography of cations.** D. A. Vyakhirev and F. N. Kulayev. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1955, **6**, 527–535; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,345.—A complete qual. analysis of cations is worked out, without preliminary separation into groups, on paper of density 75 g per cu. m. The precipitants used include NaF, NaCl, NaBr, Na_3AsO_3, Na_2SO_4, KSCN, K_2CrO_4, Na_2HPO_4, urea, 8-hydroxyquinoline, dimethylglyoxime, rubeanic acid, dithizone and alizarin. The wt. ratio of carrier to precipitant is 9:1. A drop of the soln. is transferred to a dry filter-paper saturated with precipitant. The area of the spot is $\gg$ 1 sq. cm. The nitrates of the cations were used in the experiments, the concn. of each cation being 1 mg-ion per litre. The cations, which form ppt. of varying solubility with the reagents, give an initial pptn. chromatogram, which is washed several times with a suitable solvent by touching a capillary tube containing the solvent on the centre of the spot, thereby sharpening the zone boundaries and increasing the width of the zones. With colourless ppt., the dried initial chromatogram is treated with a reagent (dithizone, rubeanic acid, alizarin, dimethylglyoxime, diphenylcarbazide, etc.), which forms with the ppt. insoluble compounds of distinctive colour. The conditions for obtaining the chromatogram and its properties for definite groups of cations are examined. With pptn. chromatograms the same laws are obeyed as in column chromatography. C. D. KOPKIN

365. **The determination of acid constituents by means of electrophoresis. I. Electrophoresis of polybasic acid radicals.** Shigeichi Achiwa (Shiga Prefectural Junior College, Hikone, Shiga-Prefecture). *J. Electrochem. Soc. Japan*, 1956, **24** (1), 13–18.—The electrophoretic (200 V) distribution of PO_4^{3-}, BO_3^{3-}, CrO_4^{2-}, AsO_4^{3-}, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ was studied on two-dimensional test

paper. The migration is greater with basic developers (*e.g.*, aq. NH_3 soln.) than with acid or neutral. The spots of polybasic acid radicals are more diffused than those of monobasic. A significant gradient of concn. was observed in the spots with change in pH. K. SAITO

366. **The influence of precipitate formation on the processes of ion exchange on a cationic ion-exchange column.** A. G. Koblyanskiĭ and N. Kh. Kameneva. *Trudy Krasnodarsk. Inst. Pishch. Prom.*, 1955, (11), 73–76; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,350.—A study has been made of the influence on cationic exchange of a ppt. formed by ion exchange on the column. In the columns (16 cm high, 8 mm diam.) was placed 2 g of air-dry cationite of granular cross-section 0·2 mm, saturated with ions of Ca, Ba or Pb. The columns were washed with soln. of suitable electrolytes (HCl, H_2SO_4, etc.); the concn. of the electrolytes were determined in successive portions of the filtrate. When a poorly-soluble ppt. is formed as the result of ion exchange between the cationite and the soln., it was established that (*i*) displacing a cation from the adsorbent takes place more actively than in a column where the ion being displaced remains in soln.; (*ii*) completeness of exchange depends on the adsorption coeff.; the greater the adsorption, the more actively does exchange take place; (*iii*) on washing the column with water, solution of the ppt. takes place. C. D. KOPKIN

367. **The use of labelled phosphate in chemical analysis. [Symposium on the use of labelled atoms in analysis.]** I. V. Tananaev and A. M. Efremova. *Izd. Akad. Nauk, SSSR*, 1955, 5–12; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,476.—A method for the determination of Al, In, La, Ce and Zr by the use of ^{32}P is based on their pptn. as phosphates and the determination of the activity of the ppt. To determine Al in magnesium alloys, add to the sample (0·1 g) 5 ml of water and conc. HCl dropwise until solution is complete. Transfer the soln. to a 10-ml centrifuge tube, rinse down the sides of the beaker with water (3 × 1 ml), add NH_4Cl (0·5 g), heat the mixture in boiling water, neutralise with aq. NH_3 (1:1) to methyl red, and heat for a further 5 min. After 10 min. centrifuge the soln., pour off the liquor (containing Mg), wash the ppt. with a 2% soln. of NH_4NO_3, and dissolve it by warming with 1 to 2 drops of HCl (1:1). To the soln. add water (1 ml), a 40% soln. of ammonium acetate (2 ml) and a 4% soln. of $K_4Fe(CN)_6$ (1 to 1·5 ml), and stir. After 30 min. centrifuge out the ppt. and wash it with a 1% soln. of KNO_3 to which has been added 1 drop of the soln. of $K_4Fe(CN)_6$. To the soln. plus wash liquor in the centrifuge tube add a soln. of $(NH_4)_2HPO_4$ or Na_2HPO_4 (0·002 g of P per ml) (3 to 5 ml), containing the labelled phosphate in sufficient quantity to give a count rate of 10,000 per min. on the pptn. of 0·1 mg of Al, and heat to boiling point. After 10 to 15 min., centrifuge out the ppt. of $AlPO_4$, wash (× 3) with a 3% soln. of NH_4NO_3, and dissolve in 1 to 2 drops of HNO_3. Transfer the soln. to a filter and determine the activity. The proportion of active to inactive P is determined each time at the same time as the determination of Al. An analogous method is used for the determination of In in the presence of Al, Fe, Mg, Ca, Mn, Zn, Cd, Cu, Tl and Ga. The Al, Fe, Ca, Mg and Mn are first pptd. by the addition of NaF (0·07 to 0·1 g of NaF to 7 to 8 ml of soln.). The phosphates of Cd, Zn and Cu are removed by soln. in aq. NH_3; Ga is held in soln. by the addition of 3 ml of a saturated soln. of ammonium oxalate, and the phosphate of Tl^{III} is soluble in excess of sodium phosphate. Satisfactory results were obtained in the determination of La and Ce (0·03 to 0·3 mg) and Zr (0·1 to 0·5 mg); Zr is pptd. as $Zr(HPO_4)_2$ from soln. containing H_2SO_4. Elements that are not pptd. in acid medium do not interfere. C. D. KOPKIN

368. **The determination of deuterium by the mass-spectrometric method.** A. MacDonald and R. I. Reed (The University, Glasgow, Gt. Britain). *Analyst*, 1956, **81**, 401–408.—A method is described for determining the deuterium content of some simple organic acids having deuterium atoms distributed about the alkyl or aryl nucleus. The dried sample is mixed intimately with dry $K_2Cr_2O_7$ and the mixture is thoroughly dried over P_2O_5. The oxidation is carried out in glass apparatus so designed that, after oxidation of the acid by heating the mixture, the water evolved can be isolated and reduced by heating with uranium. The resulting hydrogen is then introduced into a Metropolitan-Vickers M.S.2 mass spectrometer and the abundance ratio of mass 3 to mass 2 is measured at a series of different gas pressures. The discrepancy between the results and those of a reference method is 5% of the percentage abundance. The method is applicable to small amounts (0·1 to 2·0 mg) of the sample. A. O. JONES

369. **Spectroscopic determination of total water content.** H. P. Broida and H. J. Morowitz. U.S.A. Pat. 2,708,387; Date appl. 17.5.55.—A sample containing water is mixed with heavy water in which the initial H_2O to D_2O ratio (r) is about 0·99. The final molar ratio (R) is measured and the wt. fraction of water in the sample is calculated by the formula—$(R - r)V/(1 + R)M$, in which V is the vol. of heavy water and M is the mass of the sample. R and r are determined by exciting the flowing water vapour in an electrodeless discharge and scanning the light emitted with a rotating grating and a photomultiplier tube. The relative intensities of the H_α and D_α lines at 4861·3 and 4860·0 A, respectively, are proportional to the molar ratios. An accuracy within 0·1% was obtained when the method was applied to several hydrates. Application of the method to the determination of moisture in corn and other cereal products, textiles and cement is mentioned. CHEM. ABSTR.

370. **Flame-photometric determination of lithium, rubidium and caesium in silicate rocks.** E. L. Horstman (Rock Analysis Lab., Univ. Minnesota, Minneapolis, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1417–1418.—The rock sample (0·5 g) is attacked with H_2SO_4 - HF mixture and, after evaporation and dissolution of the residue in water, the ammonia group is pptd. with solid $CaCO_3$. Calcium is removed as $CaSO_4$ in aq. ethanol (1 + 1). After evaporation of the ethanol, the Li (671 mμ), Rb (795 mμ) and Cs (852 mμ) are determined by standard flame-photometric techniques; compensation is made for Na and K by the use of standard solutions. A precision of ± 10% in the 10 to 200 p.p.m. range is claimed, and a sensitivity of 5 p.p.m. for Li and Cs and 10 p.p.m. for Rb is given. D. A. PANTONY

371. **Simple determination of sodium by ion exchanger Lewatit S100.** A. Musil and H. Reimers (Univ. Graz, Austria). *Z. anal. Chem.*, 1956, **152** (1–3), 154–158.—Sodium is determined by quant.

exchange for K^+ on a pre-washed Lewatit S100 sulphonated polystyrene cation-exchanger (K form). The resin column is washed by a continuous flow of eluent in a special apparatus and the vol. of eluate is thus reduced. The K^+ in the filtrate are determined by pptn. with tetraphenylboron. The working time is 20 to 25 min. per determination and the accuracy on 8 mg of Na is within ± 1%.
J. P. STERN

372. **Colorimetric method of determining sodium in lime-soda glass by surface treatment.** K. K. Kolobova and V. A. Gerasimova (Leningrad Artistic Glass Works). *Zavod. Lab.*, 1956, **22** (7), 794–795.—Two drops of HF are placed on the glass surface (sample and standard) within a ring of paraffin wax. The solution is stirred for 5 min., two drops of water are added, and the solution, together with washings, is transferred to a platinum crucible. The solution is evaporated to fuming with one drop of dil. H_2SO_4 (1 + 3), the residue is treated with eight to ten drops of water and one drop of dil. H_2SO_4 (1 + 3) and boiled to give a clear liquid, which is transferred to a small beaker and evaporated to dryness. The residue is dissolved in the minimum amount of water, 5 to 6 ml of ethanol and 5 to 6 ml of zinc uranyl acetate reagent are added and, after 1 hr. at room temp., the ppt. is filtered off and washed first with ethanol and then with ether - ethanol mixture (2·5 + 1) until the washings give no reaction for UO_2^{2+} with $K_4Fe(CN)_6$. The ppt. and filter are dried at 60° to 70°, the ppt. is dissolved in acetic acid and determined colorimetrically with $K_4Fe(CN)_6$. The error is ± 1·5% of the content of Na.
G. S. SMITH

373. **The determination of sodium in the presence of potassium.** T. I. Kuznetsova and Z. F. Korotova. *Trudy Gos. Nauch. Inst. Khim. Prom.*, 1955, **2**, 75–81; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,511.—The use of the uranyl method for the determination of Na in the presence of K in alkaline soln. is tested. Neutralise the soln. with 0·5 *N* HCl to the indicator Tropaeolin OOO and again neutralise with 0·1 *N* HCl after simmering. The limits of the practicability of the uranyl method for alkaline soln. are made more precise with respect to the dependence on the ratio K:Na. With the ratio K:Na ≯ 3·5, the uranyl method may be used directly. With the ratio between 3·5 and 10, the method may be used after preliminary lowering of the ratio by the introduction of pure NaCl. With the ratio between 10 and 68, it is necessary to remove K from the system by pptn. as $KClO_4$. With the ratio ≃ 695, the method gives varying results. C. D. KOPKIN

374. **Synthesis of new analytical reagents for potassium and their uses. V. 2:4-Dinitronaphthosultam.** Kyoji Tôei (Chem. Dept., Faculty of Sci., Okayama Univ., Tsushima, Okayama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 670–673.—Naphthosultam is synthesised from Na 1-naphthylamine-8-sulphonate by the Dannerth method (*J. Amer. Chem. Soc.*, 1907, **29**, 1319) and nitrated with HNO_3 (sp. gr. 1·45) to yield 2:4-dinitronaphthosultam (**I**). Aq. soln. of **I** containing LiOH or Li_2CO_3 (5% **I** in 0·6% Li_2CO_3) precipitate a yellow salt of K from a neutral soln. The pptn. is quant. when the ppt. is digested for 1 hr. at room temp. The presence of Na and Mg (both in an amount greater than that equiv. to the K) causes high values. K. SAITO

375. **Polarographic micro-determination of potassium.** A. Heyrovský (Lab. II Int. Hospital, Karlova Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 69–72.—It has been stated that when K is pptd. with tetraphenylboron the K in the separated ppt. can be determined polarographically, with tetramethyl- or tetraethylammonium hydroxide as supporting electrolyte. This method has been found suitable for determining K in mineral waters, in chemically pure sodium salts and in biological material. When albumins are present (as with blood-serum and blood-plasma), they must first be removed by means of trichloroacetic acid. The specificity and sensitivity of the proposed method are greater than that of commonly used procedures. J. ZÝKA

376. **Determination of ammonium, potassium, rubidium or caesium via cationic resin exchange of their tetraphenylboron salts.** Abdel-Aziz M. Amin (Chem. Eng. Dept., Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (3), 65–66.—The tetraphenylboron salts of the alkali metals and ammonium are pptd. and dissolved in 50% acetone. The soln. of the metal salt is passed through a column of Wofatit KS, the eluate is collected in a 100-ml flask containing 0·01 *N* NaOH (25 ml), and a few drops of methyl red indicator are added. Saturated $HgCl_2$ soln. (1 ml) is added and the mixture is heated on a steam bath, then cooled, and 10% KI soln. is added to dissolve pptd. HgI_2. After the addition of 0·01 *N* HCl (25 ml), the excess of acid is titrated with standard NaOH soln. The accuracy is within ≃ ± 1·0%. C. A. SLATER

377. **The determination of copper with 8-aminoquinoline.** Yu. A. Bankovskiĭ. *Izv. Akad. Nauk, Latv. SSR*, 1955, (9), 115–119; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,514.—8-Aminoquinoline forms complex compounds with Cu, Pd and certain other elements. The least soluble is the hydrobromide of the copper complex (sensitivity 1 in 50,000), the palladium salt is slightly more soluble, and the complexes of other elements (Zn, Cd, Ni and Co) are soluble. The complex formed with Cu in the presence of HBr has the composition $[Cu(C_9H_8N_2)_2]Br_2.2H_2O$, and is pptd. as characteristic crystals, suitable for the microcrystalloscopic detection of Cu^{2+}. To determine Cu^{2+}, add an excess of a 5% soln. of 8-aminoquinoline in dilute (1:10) HBr to the acid (pH > 1) soln., containing ≮ 0·2 mg of Cu per ml, until a clear yellow colour is obtained, and allow to stand for 1 hr. Separate the large blue crystals on a glass filter No. 2, and wash with 3-ml portions of very dilute reagent soln., twice with ethanol, and finally with 5 ml and 10 ml of ether. Dry the crucible and ppt. in a vacuum-desiccator for 30 min. and weigh. The conversion factor to Cu is 0·1160. Oxidants that can oxidise 8-aminoquinoline ($Cr_2O_7^{2-}$, VO_3^-, MnO_4^-) must not be present in large quantities; Al, Zn, Ni, Cr^{III}, Co, Ce^{III}, Sn^{II} and Fe^{II} do not interfere. C. D. KOPKIN

378. **Visual titrations with diethyldithiocarbamate. IV. Determination of copper.** R. Wickbold (Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **152** (5), 338–342.—The complex of Cu with diethyldithiocarbamate (**I**), quant. pptd. from aq. soln., is sol. in $CHCl_3$. The content of Cu is determined by titration of the org. phase with aq. $HgCl_2$ (with shaking) at pH 5 to 6. The Hg - **I** complex is colourless and the end-point reached when the org. phase is just decolorised. Interference by Ni, Co, Pb and Cd is suppressed by addition of EDTA (disodium salt),

but Bi, Tl and large amounts of Pb interfere, as do CN^-. By this method 0·15 to 15 mg of Cu is determined with an accuracy within ±0·5%. *Procedure*—Add to the sample 10% aq. EDTA (disodium salt) (20 ml) and phenolphthalein soln. and make alkaline with 10% aq. NaOH. The total vol. should be ≃ 100 ml. Add 0·1 *N* **I** in portions (with shaking) and completely extract the ppt. into $CHCl_3$. Wash the org. layers with 0·1% aq. NaOH (50 ml) and re-extract the washings with $CHCl_3$. To the combined org. phases add Na acetate buffer (pH 5) (10 ml) and titrate with 0·01 or 0·001 *N* $HgCl_2$, adding the $HgCl_2$ in portions and shaking vigorously. J. P. STERN

379. **Photometric determination of copper by extraction as the diethyldithiocarbamate. Interferences and their elimination.** A. Claassen and L. Bastings (N.V. Philips Gloeilampenfabrieken, Eindhoven, Holland). *Z. anal. Chem.*, 1956, **153** (1), 30–38 (in English).—Two photometric procedures for estimating Cu with diethyldithiocarbamate described by Šedivec and Vašák (*Chem. Listy*, 1950, **44**, 103; 1951, **45**, 435) are studied to find out which elements cause interference and how the interference may be eliminated. In the first, the Cu diethyldithiocarbamate is extracted with $CHCl_3$ from an ammoniacal citrate soln. (pH ≃ 8·5) in the presence of EDTA (disodium salt). Interference is shown by Au, Pt, Os and Bi, but that due to Hg^{II}, Ag, Pd, Sb^{III}, Te^{IV} and Tl^{III} can be simply eliminated. In the second method, Cu^{2+} are extracted from an ammoniacal citrate soln. by shaking with a soln. of Pb diethyldithiocarbamate in $CHCl_3$. Only Hg^{II} in amounts > 500 μg interferes seriously, and interference due to Ag, Tl^{III} and Bi can be readily eliminated. J. H. WATON

380. **Diallythiocarbamidohydrazine [di(allylthiocarbamyl)hydrazine] as an analytical reagent. II. Determination of copper, zinc and nickel in the presence of iron and uranium.** N. K. Dutt and K. P. Sen Sarma (Univ. Coll. Sci. and Technol., Calcutta, India). *Anal. Chim. Acta*, 1956, **15** (2), 102–104.—To determine Cu^{2+} in a soln. containing a similar concn. of Fe^{3+} or up to a 5-fold excess of UO_2^{2+}, an excess of aq. NH_3 is first added, the greater part of the ppt. is redissolved by adding dil. H_2SO_4 and the remainder by adding citric acid and warming; the Cu is then pptd. as previously described (*cf. Anal. Abstr.*, 1956, **3**, 3539). When Zn is determined in similar circumstances, the ppt. produced with aq. NH_3 is redissolved by adding 3 g of citric acid and the Zn is pptd. as before (*loc. cit.*). In the separation of Ni from one-twentieth its wt. of Fe, the initial treatment is the same as for Zn and the Ni is pptd. as described previously (*loc. cit.*). W. C. JOHNSON

381. **Microgram estimation of copper and nickel by EDTA titration after paper-chromatographic separation.** I. I. M. Elbeih (Chem. Dept., Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (3), 75–77.—Copper and nickel are separated on a Whatman No. 1 paper with a solvent containing benzoylacetone (0·5 g) in *n*-butanol (50 ml) which has been equilibrated with 0·1 *N* HNO_3 (50 ml). The metals are then extracted separately from the paper with hot 50% (v/v) ethanol (15 ml) and the resulting soln. are titrated with standard EDTA (disodium salt), with murexide as indicator. At least four spots of each metal should be titrated in this way and a mean taken. The accuracy of the method for soln. containing 50 to 100 μg of each metal is within ±2%. C. A. SLATER

382. **Colorimetric determination of minute amounts of phosphorus and arsenic in metallic copper by fractional-extraction method.** Shigeru Yokosuka (Bessi Mine Office, Sumitomo Metal Mining Co. Ltd., Niihama, Ehime Prefecture). *Japan Analyst*, 1956, **5** (7), 395–398.—The extraction of the molybdates of P and As with organic solvent (*cf. Anal. Abstr.*, 1956, **3**, 686) was investigated for use in the micro-determination of P and As (both > 1 p.p.m.) in metallic Cu. The photometry of molybdenum blue obtained by the reduction of extracted heteropolymolybdate with $SnCl_2$ (1% in 0·4 *N* HCl) appears to be superior to that of the molybdate itself. The working curve is linear for < 30 μg of P and < 75 μg of As. No interference is caused by the presence of other metals, including Si and Ge. *Procedure*—The sample (10 g) is dissolved in HNO_3 (1 + 1, 80 ml), diluted to 200 ml and a 20-ml portion is adjusted to *N* HNO_3. The soln. is oxidised with NaBrO (saturated aq. soln. of Br mixed with the same vol. of water and a third of the vol. of 2% NaOH) (1 + 1, 0·5 ml) and treated with $(NH_4)_2MoO_4$ (10%, 2 ml). After 15 min., this soln. (0·9 *N* HNO_3) is extracted with 10-ml portions of a mixture of *n*-butanol (**I**) and $CHCl_3$ (1 + 3) until the organic layer becomes colourless. The organic layer is shaken with the $SnCl_2$ soln. (10 ml) and the extinction of the aq. layer is measured at 725 mμ (for P). The concn. of HNO_3 in the initial acid soln. is raised to 1·8 *N* and the soln. is extracted with a mixture of **I** and ethyl acetate (1 + 1, 20 ml). The organic layer is shaken with the $SnCl_2$ soln. (2 × 15 ml) for 30 sec. and the extinction of the aq. layer is measured at 725 mμ (for As). K. SAITO

383. **Analytical chemistry by means of oxalic acid. V. The quantitative analysis of copper and bismuth.** Masayoshi Ishibashi and Tamotsu Matsumoto (Chem. Dept., Faculty of Sci., Okayama Univ., Tsushima, Okayama). *Japan Analyst*, 1956, **5** (6), 343–346.—The pptn. of Cu and Bi with oxalic acid (or alkali oxalate) was re-examined for use in their gravimetric determination. The presence of acetic acid [>40% (v/v) for Cu; > 20% for Bi] appears to be essential for quant. pptn. of the oxalates, which are washed with ethanol and dried (Cu, 130°; Bi 120°). The concn. of Cu and Bi in the soln. from which the oxalate is pptd. must be greater than 0·1 *M* and 0·05 *M*, respectively. The presence of alkali salts vitiates the estimation.

VI. The quantitative analysis of lead and other metals. Masayoshi Ishibashi and Tamotsu Matsumoto. *Ibid.*, 1956, **5** (7), 392–394.—Similar experiments were carried out with Pb, Ni, Ag and Mn. The gravimetric determination of Pb (> 0·05 *M*) is effected by pptg. Pb oxalate at pH 3 to 7 and weighing the anhydrous salt obtained at 105°. The oxalates of Ni and Ag cannot be heated to const. weight; the pptn. of Mn oxalate is not quantitative. K. SAITO

384. **Titration of silver and iodide ions, respectively, with an end-point indication by reversible redox adsorption. I.** J. Bognár and O. Jellinek (Rákosi Mátyás Tech. Univ. for the Heavy Industries, Miskolc, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 125–140 (in English); **II.** J. Bognár and L. Nagy. *Ibid.*, 1956, **10** (1–3), 259–265 (in English).—These papers have been published in Hungarian in *Magyar Kém. Foly.*, 1955, **61** (12), 410; 1956, **62** (2), 43; *cf. Anal. Abstr.*, 1956, **3**, 1633, 2001. A. R. ROGERS

385. **Thiocyanate - cerimetric determination of silver and copper.** M. K. Joshi (Hindu Univ., Benares, India). *Z. anal. Chem.*, 1956, **152** (5), 355–357 (in English).—Silver and copper are determined by pptn. of AgSCN and of the $Cu(SCN)_2$ - pyridine complex, respectively, with excess of KSCN and back-titration with $Ce(SO_4)_2$. Thus 0·01 to 0·2 g of Ag and Cu are determined with an accuracy within ± 5%. J. P. STERN

386. **Use of complexones in chemical analysis. XLIX. Gravimetric determination of silver and mercury with mercaptobenzothiazole in presence of Complexone III.** M. Malínek and B. Řehák (Metallurg. Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 157–159.—Silver and mercuric ions, treated in ammoniacal solution with mercaptobenzothiazole (**I**), yield well-defined ppt. $[Ag(C_6H_4NCS_2)$, $Hg(C_6H_4NCS_2)_2]$, commonly used for gravimetric determinations. The selectivity of this method was increased by adding EDTA (disodium salt). *Procedure*—To the solution containing 10 to 100 mg of Ag^+ or Hg^{2+} add EDTA (disodium salt) and ammonium acetate (50%) (1 to 3 ml) and make alkaline with aq. NH_3 (phenolphthalein indicator). Heat until the solution just begins to boil and add a small excess of the reagent (5% solution of **I** in 0·5 *N* aq. NH_3). Stir the mixture, filter through a crucible (G3), wash the ppt. with 0·1 *N* aq. NH_3, dry at 110° and weigh. For masking quadrivalent cations and Be, tartaric acid should be used. The described method is suitable for determining Ag and Hg in the presence of many other metals, especially Pb and other cations that interfere in titrimetric determinations. J. ZÝKA

387. **Determination of precious metals by means of ionites.** A. B. Davankov and V. M. Laufer (D. I. Mendeleev Moscow Order of Lenin Chem.-Technol. Inst.). *Zavod. Lab.*, 1956, **22** (7), 788–789.—To determine Au (0·5 to 20 mg per litre) in soln. containing $KAu(CN)_2$ or $HAuCl_4$, the soln. is passed through a column 7 to 8 mm in diameter and 250 to 300 mm high of an anionite (type not stated) that has previously been treated with 5% HCl soln. (H_2SO_4 is used if Ag is to be extracted). The soln. (1 to 15 litres according to the concn. of Au) is passed through at a rate of 15 ml per min., or somewhat slower when large concn. of other salts or org. impurities are present. The optimum acid (HCl) concn. corresponds to pH 3·5. The issuing liquid is tested from time to time for complete extraction of Au by means of a 10% soln. of benzidine in acetic acid. The absorbent is removed from the tube, dried and ignited, and the residue is cupelled with Pb as usual. G. S. SMITH

388. **The quantitative determination of beryllium by the use of radioactive iron. [Symposium on the use of labelled atoms in analysis.]** S. V. Bleshinskiĭ and V. F. Abramova. *Izv. Akad. Nauk, SSSR*, 1955, 37–44; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,362.—Beryllium in beryl is determined by pptn. as $K_2C_2O_4.BeC_2O_4$ at pH 5 to 5·5 in the presence of excess of K oxalate and K_2SO_4 (≃ 2 *N*). To the ppt. after removal of the main bulk of liquor is added a soln. of ^{59}Fe. The activity of the soln. is measured before and after solution of the ppt. in HNO_3, and the BeO content is calculated from the formula—

$$x = 0{\cdot}0951[A - a_1 - (A - a_1 + m_k)J_2a_1/J_1a_2],$$

where A = wt. of moist ppt. + indicator (in g), m_k = quantity of HNO_3 added (in g), J_1 = number of counts per min. from a_1 g of soln. before solution of the ppt., J_2 = number of counts per min. from a_2 g of soln. after solution of the ppt. Aluminium and iron do not interfere. The Be is separated from Ca and other elements pptd. by oxalate by pptn. with aq. NH_3. In beryls containing 9·65 and 4·25% of Be, 9·61 and 4·01%, respectively, were found. C. D. KOPKIN

389. **Analytical chemistry of beryllium. VI. 8-Hydroxyquinaldine as a reagent for determination of beryllium.** K. Motojima (Fac. of Sci. and Eng., Ritsumeikan Univ., Kyoto, Japan). *Bull. Chem. Soc., Japan*, 1956, **29** (1), 29–32 (in English).—Milligram amounts of Be can be determined gravimetrically and volumetrically with 8-hydroxyquinaldine (**I**) with good accuracy. *Procedure*—To a soln. that contains 2 to 10 mg of Be, 5 ml of 4 *N* NH_4Cl and 5 ml of 10% Na tartrate are added, and the vol. is adjusted to 50 ml. After warming to between 60° and 70°, the pH is brought to ≃ 9 with 2 *N* aq. NH_3, and a 20 to 30% excess of reagent (2 g of **I** in 100 ml of 4% acetic acid) is added. The ppt. is digested for 30 min., collected on a sintered-glass crucible (porosity 4), washed with dil. aq. NH_3 (1:100) and dried at 110°. The ppt. contains 2·77% of Be. If required, the ppt. can be dissolved in hot 6 *N* HCl, and the estimation completed volumetrically with the aid of standard $KBrO_3$ - KBr and $Na_2S_2O_3$ soln. The determination may be carried out in the presence of ≃ 1 g of alkali and ammonium chlorides, nitrates, sulphates and acetates. However, those metals that give ppt. with **I** in ammoniacal soln., such as Bi, Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Ag, Ti and Zn, will interfere. Amounts of Al > 0·5 mg must be removed beforehand. Some interfering metals such as Fe, Al and Ti can be removed as their oxinates from acetic acid - acetate soln. at pH 4·5 to 5 with $CHCl_3$, together with excess of oxine. After boiling out the droplets of $CHCl_3$, Be is determined as described above.

VII. Spectrophotometric determination of micro quantities of beryllium with 8-hydroxyquinaldine. K. Motojima. *Ibid.*, 1956, **29** (1), 71–75 (in English).—The spectrophotometric determination of Be is carried out on the complex with **I** after its extraction with $CHCl_3$. *Procedure*—The slightly acid soln. of Be, containing > 30 μg in ≃ 35 ml, is treated with 5 ml of NH_4Cl soln. (10%) and 3 ml of reagent (2 g of **I** in 200 ml of 2% acetic acid). The pH is adjusted to 8·0 ± 0·2 with 2 *N* aq. NH_3. After the soln. has stood for 30 min., the beryllium complex is extracted with 10 ml of $CHCl_3$ and the extract is dried by shaking with anhyd. Na_2SO_4. The extinction of the $CHCl_3$ soln. is measured at 380 mμ against that of a blank. Gram quantities of the acetates, sulphates, chlorides and nitrates of Na, K and ammonium do not interfere in the determination, nor do < 1 mg of PO_4^{3-}, < 1·5 mg of Mg and < 5 mg of Ca. Bismuth, Cd, Cr, Cu, Co, In, Fe, Ni, Sn, Ti and Zn must be absent, and all except Ti can be removed at a mercury cathode, whilst Cu, Cd, Fe, Ni and Zn can be masked as their cyanides. The procedure may be used to determine Be in the presence of > 50 mg of Fe by making a correction for the absorbancy of Fe from measurements made at 580 mμ. The metals Al, Fe and Ti can be separated before the determination by extracting their oxinates with $CHCl_3$ as previously described.

VIII. Fluorimetric determination of micro quantities of beryllium with 8-hydroxyquinaldine. K. Motojima. *Ibid.*, 1956, **29** (1), 75–78 (in English).

—Microgram quantities of Be (0·3 to 3 μg) can also be estimated fluorimetrically by means of the complex with **I**. *Procedure*—A soln. of the beryllium complex with **I** in $CHCl_3$ is prepared as described above. The fluorescence of the $CHCl_3$ soln. is measured in a photofluorimeter, $CHCl_3$ being used for the zero setting and a quinine soln. (1 ml ≡ 1 μg of quinine sulphate) as a standard. A primary filter is used which transmits a band centred at about 360 mμ, and a secondary filter which is transparent to all wavelengths > 430 mμ, since the fluorescent light from the beryllium complex is distributed from 450 to 625 mμ. All the ions that cause interference in the spectrophotometric procedure cause interference here. Relatively large amounts of Fe and Al can be removed by extracting their oxinates with $CHCl_3$ as described above. J. H. WATON

390. **The determination of magnesium oxide in magnesium.** H. J. Allsopp (Royal Aircraft Estab., Farnborough, Hants, England). *Analyst*, 1956, **81**, 469–473.—The separation of magnesium metal from accompanying oxide is effected by sublimation of the metal *in vacuo*. An apparatus for this purpose is described and illustrated. The residue of MgO is dissolved in dil. HCl, Fe and Al are removed as hydroxides, and the magnesium content of the soln. is then determined by the use of EDTA (disodium salt) (Banks, *Brit. Abstr. C*, 1953, 3). A. O. JONES

391. **The determination of small quantities of magnesium using radioactive phosphorus.** N. I. Polevaya, N. N. Chernova and S. L. Mirkina. *Inform. Sb. Vses. Nauch. Geol. Inst.*, 1955, (1), 119–123; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,365.—To the $MgCl_2$ soln. is added a buffer soln. consisting of 2 *N* NH_4Cl and 2·5% aq. NH_3 (5:2). The active soln. of Na_2HPO_4 containing ^{32}P, with a concn. of P of 0·2 mg per ml, is added from a micro-burette in portions. After each addition the soln. is vigorously stirred for 10 to 15 min. to aid pptn. and, after allowing the $MgNH_4PO_4$ to stand for 30 min., the liquid is drawn off through a porous filter into a counter for measurement of its activity. A sharp increase in the activity of the filtrate indicates the appearance of excess of P in the filtrate, and therefore the end of the titration. By this means 0·5 to 2·5 mg of Mg was determined with an error ≯ ± 1%. Less than 0·5 mg of Mg was determined by measurement of excess activity (error 3 to 10%). The introduction of inactive primer to stimulate pptn. may be used in the radiometric titration. The introduction of inactive primer in the determination of Mg by the excess activity of the anion is not recommended because of the possibility of ion exchange between the active P of the soln. and the inactive P of the ppt. C. D. KOPKIN

392. **Rapid photometric determination of magnesium in electronic nickel.** C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1443–1445.—A 15-min. photometric oxine method for the determination of Mg in nickel is described. The metal sample (containing < 80 μg of Mg) is placed in a 125-ml flask and the total wt. of metal is made up to 100 mg with pure Ni before dissolving with mild heat in dil. HNO_3 (1:1, 2 ml). The soln. is diluted to 35 ml with H_2O, and 1 ml of $Fe(NO_3)_3$ soln. (4%) and 1 ml of $(NH_4)_2S_2O_8$ soln. (1%) are added. Aq. NH_3 (sp.gr. 0·90) is added dropwise (1 ml in excess) to precipitate Fe. The solution is heated to 65° and filtered rapidly into a separating funnel. After cooling, aq. NH_3 (sp.gr. 0·90; 10 ml), NaCN (10%, 5 ml), aq. 2-butoxyethanol (1:1, 5 ml) and oxine solution (20 ml) are added successively and the extraction and measurement procedure is carried out according to Luke and Campbell (*Anal. Abstr.*, 1955, **2**, 872). E. G. CUMMINS

393. **Paper-chromatographic separations of cations. I. Separation of alkaline-earth chlorides in the solvent system tetrahydrofuran - water - hydrochloric acid.** H. Hartkamp and H. Specker (Inst. Spectrochem., Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 107–112.—The R_F values of Be, Mg, Ca, Sr and Ba in various mixtures of aq. HCl and tetrahydrofuran (**I**) have been systematically determined and plotted. It is shown that for a separation of all these ions, soln. of 1·2 to 3·7 *N* HCl [30% (v/v) in **I**] or of 7·4 to 12 *N* HCl [70% (v/v) in **I**] are most useful. J. P. STERN

394. **Analysis of alkaline earths. II. Separation and determination with the aid of precipitation exchange and complex formation by EDTA.** H. Ballczo and G. Doppler (II Chem. Lab., Univ. Vienna). *Z. anal. Chem.*, 1956, **152** (5), 321–337.—The solubilities of the salts of Ba, Ca and Sr, particularly sulphates, oxalates and chromates, in aq. soln. of EDTA (1 equiv.) between pH 1 and 10 are examined and the results are applied to the separation of the cations. A procedure is developed for the separation of Ba as chromate and of Sr and Ca as oxalate, Sr being converted into $SrCO_3$ and the oxalate liberated being determined with $KMnO_4$. The accuracy of the determinations is within ± 1%. *Procedure*—To the sample (free from H_2S) add 0·5 *M* EDTA (disodium salt) (10 to 12 ml) and adjust to pH 5 (total vol. ≃ 100 ml). Heat to boiling and add dropwise aq. $(NH_4)_2CrO_4$ (1 to 2 g in 10 ml). Set aside for 30 min. and filter. Wash with a little cold water and either dry the $BaCrO_4$ at 180° or determine the Ba in the solid by dissolving it in $HClO_4$, reducing with excess of $FeCl_2$ and titrating the excess with $KMnO_4$. Acidify the filtrate from the $BaCrO_4$ and warm (when violet Cr^{III} - EDTA is formed). Add solid ammonium oxalate (2 g) to give a clear soln. and then ammonium acetate soln. as buffer to a pH of 3·5 to 4 (adjusted to pH meter). Set aside in the cold for 4 hr. and filter. Wash with 1% ammonium oxalate and then with water (10 ml). Treat the residue with 0·1 *N* K oxalate and 0·2 *N* K_2CO_3 (exchange soln.) on the steam bath for 30 min., add H_2SO_4 (1:4) (4 ml) and titrate with 0·1 or 0·01 *N* $KMnO_4$ (ferroin indicator). Repeat the exchange pptn. (blank titration) and the difference in titre corresponds to the content of Sr. Dissolve the residual Ca oxalate ppt. in H_2SO_4 (1:4) (4 ml) and water and titrate at 50° to 60° with $KMnO_4$. J. P. STERN

395. **Ames laboratory analytical procedures for determination of impurities in calcium metal.** C. V. Banks and B. D. LaMont (Iowa State Coll., Ames, Iowa, U.S.A.). *U.S. Atomic Energy Comm.*, 1955, 15C–584, 17 pp.—The determination of Al, Cr, Fe, Mn, Ni, N and Si in calcium metal is described. Iron is determined spectrophotometrically by measuring the extinction of the reddish-orange colour of the tri(1:10-phenanthroline) - Fe^{II} ion at 515 mμ. This complex effectively removes the interference from Fe, and Al is determined spectrophotometrically at 395 mμ in the soln. remaining from the determination of Fe

by extracting it with a $CHCl_3$ soln. Chromium is determined polarographically. The diffusion current of the first Cr wave, occurring at − 1·0 V *vs.* the S.C.E. in *M* $CaCl_2$, is directly proportional to the concn. of Cr. Manganese is determined by oxidation to MnO_4^- with KIO_4, and the extinction of the MnO_4^- is measured spectrophotometrically at 545 mμ *vs.* a water blank. Nickel is determined spectrophotometrically as the Ni^{II} - glyoxime complex in an $(NH_4)_2HC_6H_5O_7$ soln. Gum arabic is used as a stabilising agent. Nitrogen is determined by the standard Kjeldahl procedure. Silicon is determined spectrophotometrically as the heteropoly molybdenum-blue complex at 815 mμ.

CHEM. ABSTR.

396. **Determination of small amounts of calcium with iodanilic acid hemi-ether.** L. Jankovits (Dept. of Gen. Chem., Tech. Univ., Budapest, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 99–110 (in German).—The decrease in the intensity of the purple colour of an aq. soln. of the sodium salt of the hemi-ether of 2:5-dihydroxy-3:6-di-iodo-1:4-benzoquinone (**I**) in the presence of Ca^{2+} forms the basis of a rapid method of determination of small amounts of calcium. Many cations interfere. *Procedure*—Neutralise the sample (containing 0·4 to 2 mg of Ca^{2+}), dilute with H_2O to 30 ml, add a 0·3% aq. soln. of **I** (10 ml) and shake at 30-min. intervals for 4 hr. Dilute with H_2O to 50 ml, filter and compare the extinction with H_2O at 530 mμ. Calculate the concn. of Ca^{2+} by the use of a calibration curve. A. R. ROGERS

397. **Determination of small amounts of calcium in pickling salt.** A. L. Gol'dinov and B. S. Roginskaya. *Zavod. Lab.*, 1956, **22** (7), 801–802.—The calcium in the solution of the salt is absorbed in a column of cationite. It is then extracted with HCl and determined by means of titration with EDTA. G. S. SMITH

398. **Rapid determination of CaO (in effect CaO plus MgO) in a fat lime, by thermogravimetry.** P. Remy-Genneté and B. Audouze (Lab. de Chim. Ind., Fac. des Sci., Clermont-Ferrand, France). *Bull. Soc. Chim. France*, 1956, (6), 955–957.—Although the assay of lime by slow slaking with excess of water and observing the loss of weight on drying has been previously reported by other workers, they used a higher temp. which could cause decomposition of the $Ca(OH)_2$ and took no account of the possible take-up of CO_2 from the atmosphere. *Procedure*—A sample of lime that has been finely ground and stored in a closed vessel is put into a small weighed crystallising dish which is placed on the pan of the thermobalance with the i.r. heating lamp switched on. The weight is noted. The lime is then carefully slaked with excess of water and replaced in the thermobalance. Weight is plotted against time while heating at 150° to 200°. Constant weight indicates the increase due to the reaction $CaO + H_2O = Ca(OH)_2$, but the sample is held in the balance to determine the rate of take-up of CO_2 and a correction made if necessary. The method is compared with the "phenol method."

E. J. H. BIRCH

399. **X-ray diffraction powder patterns of the calcium phosphates.** A. O. McIntosh and W. L. Jablonski (Central Res. Lab., Canadian Industries, Ltd., McMasterville, Quebec, Canada). *Anal. Chem.*, 1956, **28** (9), 1424–1427.—The X-ray powder patterns of 15 calcium phosphates are described, with a view to identification of phosphate materials.

D. A. PANTONY

400. **Photometric titration of small amounts of barium with (ethylenedinitrilo)[ethylenediamino]-tetra-acetic acid.** A. I. Cohen and L. Gordon (Dept. of Chemistry, Syracuse Univ., Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1445–1447.—The soln. containing 0·05 to 12 mg of Ba^{2+} is adjusted to pH 11 (aq. NH_3 - NH_4Cl buffer) and treated with Phthalein Purpur indicator (phthalein complexone) (*cf. Anal. Abstr.*, 1954, **1**, 1180). The soln. is titrated spectrophotometrically at 570 mμ with 0·002 to 0·01 *M* EDTA (disodium salt) and a correction is made for a blank. D. A. PANTONY

401. **Gravimetric assay of barium thiosulphate monohydrate.** W. L. W. Ludekens and N. R. de Silva (Univ. of Ceylon, Colombo). *Chemist Analyst*, 1956, **45** (3), 77.—The method described depends on the oxidation of the $S_2O_3^{2-}$ to SO_4^{2-} by means of bromine water. The SO_4^{2-} so formed are estimated by adding an excess of Ba^{2+} and weighing the pptd. $BaSO_4$ after ignition in the usual way. The standard deviation of 5 determinations was ± 0·03%.

C. A. SLATER

402. **A semi-quantitative method of spot analysis for zinc.** N. F. Maĭorov. *Zap. Leningrad Gorn. Inst.*, 1955, **30** (2), 192–202; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,524.—A semi-quant. method for the spot determination of Zn with dithizone is worked out. First determine the quantity of carbonates present. Place 1 g of sample in a quartz or porcelain crucible and add 4 ml of 10% H_2SO_4. Neutralise the carbonates by the addition of 40 to 50% H_2SO_4. Cover the crucible with a watch-glass and boil on a sand bath for 10 min. Then add water to give the original vol. Allow any residue to settle, transfer a drop of the liquor to a filter-paper (ashless), which is placed in ammonia vapour for 15 min. Then add a drop of a 0·1 to 1% soln. of dithizone in $CHCl_3$. The appearance of a crimson colour indicates the presence of Zn. Then every 15 to 20 sec. add to the reaction spot further drops of dithizone soln. of the same concn. until the crimson colour of the spot changes to green or dark green. The number of drops of soln. required to cause this change gives the content of Zn, by the use of a calibration curve. By this method from 0·00005 to 1% of Zn can be approx. determined. C. D. KOPKIN

403. **The determination of small quantities of zinc.** R. Kalinowska and J. Siedlecka. *Roczn. Państw. Zakl. Hig.*, 1955, **6** (2), 93–107; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,367.—In the colorimetric determination of Zn in food products by the use of dithizone, Cu and Sn^{2+} interfere. The Cu is extracted as its dithizone complex in an acid medium, and the Sn^{2+} are oxidised to Sn^{4+}. Heat the sample (flour, milk powder, etc.) (2 g) at 450° for 3 hr. Moisten the residue with 10% NH_4NO_3 soln. (1 ml), dry and bake once more for 3 hr. Moisten the ash with conc. HCl (0·5 ml) and twice-distilled water (15 ml), add 5 to 7 drops of H_2O_2 and evaporate the soln. to dryness. Dissolve the dry residue in conc. HCl (0·5 ml) and water (15 ml), and warm for 20 min. on the water bath. After cooling, neutralise to methyl red with *N* aq. NH_3 to a yellow colour. Add *N* HCl (2 ml), transfer the soln. to a Pyrex-glass separating funnel and extract the Cu with 20 ml of 0·03% dithizone in CCl_4 for 3 min. Wash the aq. phase, containing Sn, with CCl_4 (10, 8 and 5 ml), add a drop of methyl red and dilute the soln. to 100 ml. Add to a 10-ml aliquot a citrate buffer soln. (prepared by mixing 500 ml

of 0·5 *M* ammonium citrate soln. and 70 ml of *N* aq. NH_3 and diluting to 2 litres) (20 ml), 0·2% Na diethyldithiocarbamate soln. (2·5 ml) and a soln. of dithizone in CCl_4 (40 mg per litre) (20 ml). Shake for 30 sec. After separating the layers, add to 10 ml of the organic phase dilute aq. NH_3 (1 in 200) (30 ml), shake for 15 sec., and measure the extinction in a Klett colorimeter, with a green filter. The quantity of Zn present is determined from a calibration curve, constructed by using various quantities of standard 0·01% Zn soln. The sensitivity of the method corresponds to 1 μg of Zn. The mean error is $\pm$ 5%. C. D. KOPKIN

404. **The volumetric determination of zinc by the use of citrates.** A. V. Pavlinova and B. I. Bernshteĭn. *Nauk. Zap. Chernived'k Univ.*, 1955, **11**, 107–112; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,369.—In the reaction of Zn with alkali-metal citrates, one atom of Zn releases one equiv. of acid, the titration of which determines the Zn. To obtain accurate results it is necessary to add excess of citrate, titrate to thymolphthalein and add at the end of the titration an excess of $CaCl_2$, so as to give a concn. of 0·2 to 0·6%. The method is no less accurate than the well-known ferrocyanide method, but more convenient, as no ppt. is formed in the reaction. C. D. KOPKIN

405. **The volumetric determination of zinc with potassium ferrocyanide with reversible redox-adsorption indicators.** J. Bognár and L. Nagy (Rákosi Mátyás Tech. Univ. for the Heavy Industries, Miskolc, Hungary). *Magyar Kém. Foly.*, 1956, **62** (7), 217–220.—Xylene blue VS and Patent blue V (or Azure blue S) are used in the determination of Zn with $K_4Fe(CN)_6$ (**I**). In the presence of $K_3Fe(CN)_6$ (**II**), the colour of the indicators adsorbed on the surface changes from red to green, or greenish blue when excess of **I** is added. The indicators cannot be oxidised in soln. *Procedure*—Dilute a soln. containing $\leq$ 10 mg of Zn to 50 ml; add 0·3 ml each of a 0·1 *M* soln. of **II** and a 0·1% aq. soln. of the indicator. Titrate slowly with 0·025 *M* **I** till the greenish colour persists for 2 to 3 min., wait until the pink colour returns and then either heat to boiling point and titrate to the final colour-change, or add **I** in an excess of 0·1 to 0·3 ml and back-titrate at 50° to 60° with standard zinc soln. The latter method gives a sharper end-point and can be used down to pH 2; NH_4^+ do not interfere in the back-titration method. The soln. of **I** is standardised against a zinc soln. of similar concn. The amount of the indicator present greatly affects the vol. of **I** consumed. A. G. PETO

406. **Spectrographic methods for the analysis of solutions. I. Determination of components in zinc and magnesium alloys.** W. Kemula, W. Brachaczek and A. Hulanicki (Zaklad Chem. Nierorg. Univ., Warsaw). *Przem. Chem.*, 1955, **11**, 679–683.—The features of several existing techniques of spectrographic analysis were compared; continuous spraying of the solution of the tested material into the excitation zone was considered to be the most satisfactory. A simple and easily operated instrument for this purpose is described. Several materials were tested for their suitability as electrodes (carbon, copper), but silver was preferred. The pressure of air (controlling the quantity of solution sprayed) was found to affect the character of the spectrum obtained. The effect of changing the analytical spark gap was also investigated. The intensity of lines was better with a 5-mm gap than with a 3-mm one and the electrodes were less contaminated when the larger gap was used. The concn. of inorganic ions also had a marked effect on sensitivity and precision of results. The best results were obtained with a concn. of 2%. The following ranges of concentrations of metals in magnesium alloys were determined—Al 2 to 12%, Mn 0·1 to 1·5%, and Zn 0·2 to 0·6%, with coefficients of variation of 2·9%, 4·7% and 4·0%, respectively. The analytical lines used were—Al, 3082 A; Mn, 2943 A (with the 3096-A Mg line as internal standard); and Zn, 2138 A (with the 2134-A Ag line as internal standard). Magnesium present in zinc as an impurity was determined in the range 0·005 to 1% with a coefficient of variation of 4·9% when 0·0002% of Be was used as internal standard (analytical lines were Mg, 2802 A; Be, 3130 A). The presence of Al in concn. of 1 to 20% was found to cause a serious shift in the calibration curve for Mg when Be was used as internal standard. K. F. SPOREK

407. **Measurement of the amount of zinc co-precipitated with hydrated ferric or chromic oxide.** Michio Mashima (Faculty of Eng., Niigata Univ., Nagaoka, Niigata Prefecture). *Japan Analyst*, 1956, **5** (6), 324–326.—Co-pptn. of Zn with $Fe(OH)_3$ or $Cr(OH)_3$ from an HCl soln. was studied with the aid of radioactive ^{65}Zn. The absolute amount of co-pptd. Zn increases markedly with increase in the amount of Zn, its percentage approaching a const. value (11% for 10 to 40% of Zn in Fe). There is a similar trend in the co-pptn. with $Cr(OH)_3$, but to a slightly less extent. K. SAITO

408. **Determination of small amounts of iron in zinc sulphide by a luminescence method.** É. M. Pesochinskaya (Leningrad Chem. Reagent Works "Red Chemist"). *Zavod. Lab.*, 1956, **22** (7), 789–791.—To determine Fe (5×10^{-7} to $1{\cdot}5 \times 10^{-6}$ g per g) in ZnS activated by Ag the sample is irradiated with light of 365 μ and the relative intensity of the max. of the blue band (450 μ) to the max. of the red band (640 μ) is measured. The content is read from a calibration curve. The intensity of the red band given by Ni at the same place as Fe is low in comparison with that of Fe. G. S. SMITH

409. **Visual titrations with diethyldithiocarbamate. V. Determination of cadmium.** R. Wickbold (Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **152** (5), 342–345.—Addition of CN^- limits the metals pptd. by diethyldithiocarbamate (**I**) to Pb, Bi, Tl and Cd. The Cd-**I** complex is pptd. at pH 11 to 12 and extracted into $CHCl_3$ and the **I** (equiv. to the Cd) in the org. phase is determined by adding Cu^{2+} as indicator and titrating with $HgCl_2$ (cf. *Anal. Abstr.*, 1957, **4**, 378) until the org. phase is colourless (*i.e.*, contains Hg-**I** complex only). Thus 1 to 30 mg of Cd is determined with an accuracy within $\pm$ 0·5%. The method is useful for the determination of Cd in galvanising baths. Lead, Bi and Tl interfere as they react analogously. J. P. STERN

410. **Visual titrations with diethyldithiocarbamate. II. Determination of mercury.** R. Wickbold (Chem.-Werke Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **152** (4), 262–266.—Of all heavy metals, Hg forms the least sol. complex with Na diethyldithiocarbamate (**I**) and, on addition of **I** to a mixture of Hg and other metals (*e.g.*, Cu), the colourless Hg-**I** complex is pptd. first and the coloured complexes of

the other metals are formed only when all the Hg has been complexed. These metals, and particularly Cu (yellow complex), can thus be used as indicators in a titrimetric procedure for determining Hg. Recognition of the end-point is facilitated by addition of chloroform and vigorous shaking. In colourless soln. a sharper end-point is obtained by emulsification of the chloroform - water mixture. Only Ag^+, CN^- and I^- interfere. The presence of Cl^-, Br^- or SCN^-, which themselves form slowly dissociated complexes with Hg, reduces the rate of reaction. The accuracy for 1·5 to 400 mg of Hg is within ± 0·5%. *Procedure*—Add to the sample 10% aq. tartaric acid (10 ml), 0·1% Cu acetate indicator (1 ml) and aq. NH_3 until alkaline. Then add 10% Marlipal MG emulsifier (1 to 2 ml) and chloroform (a few ml). Shake the stoppered flask vigorously (forming a white emulsion). Titrate with 0·1 (or 0·01) *N* **I** until the emulsion just shows a yellow colour; simultaneously standardise the labile soln. of **I**. If the sample is coloured, omit the emulsifier and use more chloroform (10 ml).

J. P. STERN

411. **The volumetric determination of mercury with the aid of acid - base indicator. Determination of mercury in brine-electrolysis muds.** Shizo Hirano and Masami Suzuki (Inst. of Techno-anal. Chem., Faculty of Eng., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1956, **5** (7), 375–378.—Experimental conditions for the acidimetric analysis of Hg by the use of acetone and KI (*cf. Anal. Abstr.*, 1954, **1**, 225) was studied for application to the determination of Hg (< 0·5%) in waste mud from the mercury process for the electrolysis of aq. NaCl. The whole procedure should be carried out in an atmosphere free from CO_2, and in the absence of Zn, Cd and Ag. *Procedure*—The sample is dissolved in 6 *N* HCl and H_2O_2 (30%, 1 to 2 ml) and air is bubbled through to remove Cl. A portion is treated with hydrazine (a few grams) and diluted to give a 0·3 *N* soln. to precipitate HgS, which is dissolved in a mixture of HNO_3 and HCl (3 + 1) (3 ml). This soln. is diluted to ≃ 100 ml, bubbled with air free from CO_2 and neutralised to phenolphthalein with 2 *N* NaOH. Another 0·3 ml of NaOH is added to precipitate HgO, which is dissolved by adding acetone (10 ml). This product is exactly neutralised with 0·02 *N* H_2SO_4, treated with KI (> 3 g for 0·2 g of Hg) and the resulting OH^- are titrated with 0·02 *N* H_2SO_4. When Cu is present, tartaric acid is added.

K. SAITO

412. **Spectrophotometric determination of micro quantities of boron.** J. F. Possidoni de Albinati and R. H. Rodríguez Pazqués (Anal. Chem. Div., National Atomic Energy Admin., Argentina). *An. Asoc. Quim. Argent.*, 1955, **43** (4), 215–226.—The colorimetric determination of B based on the red colour formed by the reaction between H_3BO_3 and curcumin in the presence of oxalic acid (*cf.* Scott and Webb, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 180) is discussed and a technique is described for the determination of B in compounds of U and in graphite. Experimental results showed that (*i*) it is critically important that the drying time is constant for all determinations, as otherwise results vary widely; and (*ii*) since the colour intensity is higher with shorter drying times, it is preferable to use a metal of high thermal conductivity, *e.g.*, Pt, for the container. The sensitivity of the method is found to be 0·00014 μg per sq. cm with a 10-mm light path, and the error was less than 0·06 μg for a sample containing 0·1 to 5 μg.

D. LEIGHTON

413. **Analytical use of the ^{27}Al (α, n) ^{30}P reaction.** E. Odeblad and S. Odeblad (Karolinska Inst., Sabbatsbergs Hospital, Stockholm, Sweden). *Anal. Chim. Acta*, 1956, **15** (2), 114–117.—Substances containing Al are irradiated with a ^{210}Po alpha source. The induced activities are measured with a Geiger - Müller counter or the pulses are visualised on a cathode-ray oscilloscope and recorded on moving film. A close experimental relationship is established between the content of Al and the count, but B must be absent and Mg must not be present in appreciable amounts.

W. C. JOHNSON

414. **Complexiметric titration of aluminium and iron and of their sum.** H. Flaschka and H. Abdine (Nat. Res. Council, Dokki-Cairo, Egypt). *Z. anal. Chem.*, 1956, **152** (1–3), 77–85.—The determination of Fe and Al (and of their sum) is performed in cold and boiling aq. acetic acid, respectively, at pH 3 by titration with EDTA (disodium salt) and with 1-(2-pyridylazo)-2-naphthol (**I**) and a trace of Cu as indicator. The accuracy on 2 to 25 ml of 0·01 or 0·1 *M* soln. is within ± 0·02 or 0·05 ml, respectively. No interference is caused by Ca, Mg, Mn or Ti. *Procedure*—Partly neutralise the strongly acidic sample with aq. NH_3 (to pH ≯ 1), add a little 0·1% ethanolic bromophenol blue indicator and then 10% aq. ammonium acetate until the colour changes to greyish blue. Add rapidly acetic acid (5 ml) when the pH should be 3. If the soln. contains Fe, add a little salicylic acid and titrate slowly with 0·01 or 0·1 *M* EDTA (disodium salt) to a yellow colour. Then heat to boiling point and add sufficient **I** (0·1% ethanolic soln.) and 1 to 2 drops of 0·1 *M* Cu - EDTA to give a violet colour. Titrate with EDTA (disodium salt) with stirring until the yellow colour is stable (red does not reappear within 30 sec.).

J. P. STERN

415. **Direct photometric determination of aluminium in iron ores.** U. T. Hill (Inland Steel Co., E. Chicago, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1419–1424.—The iron ore (0·2 g) is fused with Na_2CO_3 and the cooled melt is extracted with dil. HCl. To an aliquot of the soln. is added Na thioglycollate soln. and Eriochrome cyanine R soln. Absorption is measured at 535 mμ with respect to a blank that has been treated with EDTA (disodium salt) after adjusting each to pH 6 with ammonium acetate buffer. Allowance is made for the iron and vanadium background absorptions. Beer's law holds for contents of Al up to 10%, and data are presented to illustrate the accuracy of the method.

D. A. PANTONY

416. **Separation of aluminium and zirconium by the method of ion exchange.** Yu. I. Usatenko and L. I. Gureeva (Dniepropetrovsk Chem. Technol. Inst.). *Zavod Lab.*, 1956, **22** (7), 781–783.—The absorptive properties of five cationites—sulpho-coal, Wofatit R, KU-1, SBSR and MSF-1—for Zr^{4+} and Al^{3+} as affected by the pH of the solution are determined. The max. normalities of HCl at which complete absorption occurs are 0·25, 0·25, 0·75, 0·75 and 0·25, respectively, for Al^{3+}, and 1·0, 0·75, 1·5, 1·25 and 1·0, respectively, for Zr^{4+}. Sulpho-coal, and somewhat less favourably KU-1, can be used for quant. separation of Zr^{4+} and Al^{3+}.

G. S. SMITH

417. **Separation of aluminium phosphate minerals from kaolinite by selective solution.** I. May and R. Smith (U.S. Geol. Surv., Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 766–768.—Wavellite, crandallite and millisite

(minerals ordinarily present in the Florida pebble phosphate deposits) are completely decomposed by boiling for 20 min. with HCl (1 + 1), whilst only 1% of the Al present in kaolinite is thus dissolved.
A. A. ELDRIDGE

418. **Polarographic half-wave potentials. V. Half-wave potentials of gallium.** K. Micka (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 43–45.—The existing literature on the polarographic behaviour of Ga was studied and, using the three-electrode system, the half-wave potentials in various supporting electrolytes were exactly measured. The best developed waves have been found in ammoniacal buffer solution (*M* aq. NH_3 - *M* NH_4Cl, 5 *M* aq. NH_3 - *M* NH_4Cl). In slightly acid, not buffered solutions, the wave for Ga is accompanied by a wave for H^+, which can be removed by neutralising with hydroxide. The oscillopolarographic behaviour of Ga was also studied and it was found that, depending on the medium, characteristic and various cathodic or anodic cuts-in appear on the curves.
J. ZÝKA

419. **Spectrographic determination of gallium in bauxites.** T. Kotsis and A. Huber. *Kohászati Lapok*, 1955, **10**, 184–186.—A quant. spectrographic procedure has been devised for the determination of gallium in bauxites by the use of solutions. Bauxite (2·5 g) is fused with five times its weight of KOH in a silver crucible. The melt is extracted with water, washed into a beaker while hot, then boiled and filtered hot. The ppt. is washed with a 1% KOH soln., the filtrate being made up to 50 ml with water. This soln. (2 ml) is mixed with 0·5% standard soln. of Mo (1 ml) and used directly for arcing. An a.c. arc of 3 amp. and the reference lines Ga 4172·06 - Mo 4232·61 A and Ga 2874·2 - Mo 2871·5 A are used.
LIGHT METALS BULL.

420. **Determination of indium with hexa-amminocobalt(III) chloride.** Tomitaro Ishimori and Kaoru Ueno (Chem. Dept., Faculty of Sci., Kyushu Univ., Hakozaki, Fukuoka). *Japan Analyst*, 1956, **5** (6), 329–331.—Indium is pptd. with hexa-amminocobaltic chloride (**I**) as $[Co(NH_3)_6]InCl_6$ from 4 *N* HCl, washed with 2 *N* HCl (Eusslin, *Metall und Erz*, 1941, **28**, 305; *Z. anorg. Chem.*, 1942, **249**, 119) and dissolved in hot water to be determined by colorimetric (1 to 50 mg of In), volumetric (0·3 to 70 mg) or radiochemical (5 to 50 μg) methods. The orange colour of the Co complex obeys Beer's law for < 50 mg of In per 50 ml. The ppt. is washed with ethanol to remove the adsorbed 2 *N* HCl, then dissolved in hot water, and a portion is titrated with $AgNO_3$ by the Volhard method. By the use of radioactive **I** containing ^{60}Co, radiochemical analysis is effected by a direct measurement of the activity of the washed ppt. Interference results from the presence of Cd (> 1·5 mg), Tl (>12·4 mg) and Fe (> 30 mg).
K. SAITO

421. **Organic co-precipitants (collectors). Co-precipitation of indium.** V. I. Kuznetsov and G. V. Myasoedova. *Primen. Mech. Atom. v Anal. Khim., M., Izd. Akad. Nauk SSSR*, 1955, 24–28; *Ref. Zhur., Khim.*, 1956, Abstr. No. 10,085.—By conversion of indium into iodide and treatment with methyl violet soln. a ppt. is formed which contains all the In present down to 1 μg in 20 litres. By limiting the amount of I^- added, other elements that form insoluble iodides may be removed and the In determined in the filtrate. To 250 ml of dil. H_2SO_4 (0·2 to 0·5 *N*) containing In and ≯ 150 mg of elements reacting with I^-, add NH_4I (≯ 2 g), shake and add dropwise 25 ml of aq. methyl violet soln. (6%). Filter after 20 to 30 min. and wash with 50 to 100 ml of wash soln. (150 ml of 0·5 *N* H_2SO_4, 0·25 ml of methyl violet soln. and 0·05 g of NH_4I). To the filtrate add 35 g of NH_4I and, dropwise, 10 ml of methyl violet soln. Filter, wash with 30 to 50 ml of wash soln., dry and ignite at 350° to 450°.
R. LORD

422. **Use of amines in inorganic polarography. III. Polarographic determination of indium and cadmium in solutions containing diaminoethane.** J. Doležal (Inst. Anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 54–61.—The polarographic determination of In in a diaminoethane medium, or in combination with other supporting electrolytes, was studied. In alkaline medium, it is possible to determine In and Cd simultaneously. In the determination of a mixture of Cd, In and Zn, an electrolyte consisting of a mixture of diaminoethane, phosphate and cyanide is necessary. Indium and cadmium can be determined even in a 500-fold excess of zinc. The half-wave potentials of many other elements in the same and similar mediums were measured and possible applications to analysis discussed.
J. ZÝKA

423. **Micro-gravimetric determination of thallium with thionalide [thioglycollic acid 2-naphthylamide].** C. Cimerman and G. Selzer (Israel Inst. Technol., Haifa, Israel). *Anal. Chim. Acta*, 1956, **15** (3), 213–217.—From 3 to 6 mg of Tl can be determined, with a max. error of ± 0·4%, by pptn. at 80° with a soln. of thionalide (25 to 35 mg) in acetone, in the presence of 10% Na acetate (0·5 ml), 20% KCN (0·25 ml) and 2 *N* NaOH (0·5 ml). The soln. should be stirred vigorously during the dropwise addition of the reagent. After cooling, the soln. is filtered through a porcelain filter-stick, Emich's micro-technique being adopted. The washed ppt. is dried at 110° and weighed.
W. J. BAKER

424. **The thermolysis of the 8-quinolinol [8-hydroxyquinoline] chelates of yttrium and the rare-earth elements.** W. W. Wendlandt (Texas Technol. Coll., Lubbock, Texas, U.S.A.). *Anal. Chim. Acta*, 1956, **15** (2), 109–113.—When La is pptd. with 8-hydroxyquinoline by the method of Pirtea (*Brit. Abstr. A*, 1937, 47) the resulting complex contains free 8-hydroxyquinoline, which is shown in a thermolysis curve to be lost gradually between 50° and 220°. If the complex is obtained by the method of homogeneous pptn. (Willard, *Brit. Abstr. C*, 1951, 155) it contains no free 8-hydroxyquinoline, and the thermolysis curve shows (*i*) an approx. horizontal portion up to 350°, (*ii*) loss of the organic material while the temp. rises from 350° to 525° and (*iii*) formation of La_2O_3 at 700° to 800°. The 8-hydroxyquinoline complexes of Ce^{III}, Pr, Nd, Sm, Gd and Y prepared by homogeneous pptn. yield thermolysis curves similar to that of the lanthanum complex pptd. by the same method.
W. C. JOHNSON

425. **Stepwise elution analysis for the separation of rare-earth metals. Preliminary communication.** A. Almásy (Inst. Res. in Heavy Industry, Veszprém, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 303–306 (in English).—Experiments on the stepwise elution of rare-earth metals from Dowex-50 (H^+ form) with a soln. containing *M*

lactic acid, 0·1 *M* phenol and various amounts of NH_3 showed that the rate of elution as a function of pH undergoes a sudden change at a given pH value, which is different for each metal. The method is demonstrated by the separation of Yb, Ho, Eu, Sm, Pr and La. A. R. ROGERS

426. **The quantitative separation of small quantities of rare-earth elements from uranium fission products.** L. Hartinger and L. Holleck (Chem. Inst. der Hochschule, Bamberg, Germany). *Angew. Chem.*, 1956, **68** (12), 412.—The separation of rare-earth elements from uranium fission products on ion-exchange resins, with nitrilotriacetic acid as complexing agent, was investigated on quantities ranging from a fraction of a milligram to 10 mg. With fine-grain or "colloidal" resins, good separation was achieved without close control of pH. With a 59-cm column of diameter 0·6 cm, containing coarse-grain (0·25 to 0·5 mm) resin, Nd and Pr could not be separated at pH 5·1, but Y, Sm (Pm), Nd and Pr were quantitatively separated at pH 4·14 to 4·20. A. B. DENSHAM

427. **Paper chromatography of inorganic ions. XIV. Separation of gadolinium-group rare earths.** M. Lederer (Inst. du Radium, Paris). *Anal. Chim. Acta*, 1956, **15** (2), 122–124.—A solvent composed of ethanol (90 ml), 2 *N* HCl (10 ml) and NH_4SCN (1 g) is used for the separation of the gadolinium group of rare earths by paper chromatography with a development time of 48 hr. Complete separation of Nd, Sm and Eu is achieved; Eu, Gd and Tb overlap, but Eu can be separated from Tb. The solvent does not separate the yttrium earths. W. C. JOHNSON

428. **Quantitative separation of cerite rare-earth elements by ion exchange and the effect of the pH of the eluent.** L. Holleck and L. Hartinger (Chem. Inst. der Hochschule, Bamberg, Germany). *Angew. Chem.*, 1956, **68** (12), 411–412.—The separation of rare-earth elements on the cationic ion-exchange resin Nalcite HCR, with nitrilotriacetic acid as complexing agent, has been described earlier (*Ibid.*, 1954, **66**, 586). It is now found that Sm, Nd, Pr and La form two types of complex at low and medium pH values. The best separations are obtained in the intermediate region, and the metals mentioned above can be separated quantitatively by eluting in turn at pH 3·50, 3·75, 3·80 and 4·20. A. B. DENSHAM

429. **Oscillopolarographic investigation of depolarising effect of lanthanum(III) ions.** L. Treindl (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 154.—It was observed that La^{3+}, even in 4×10^{-4} *M* concn. in 0·2 *M* to 1 *M* KI, NaI or tetramethylammonium hydroxide, in the presence of oxygen, yield a cathodic and anodic cut-in on $dV/dt = f(V)$ curves. The presence of Zn^{2+} does not cause interference, because its depolarising potential is more positive (300 mV). J. ZÝKA

430. **Concentration of microgram amounts of rare earths in thorium. Precipitation and ion-exchange procedures.** L. Gordon, F. H. Firsching and K. J. Shaver (Syracuse Univ., Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1476–1479.—Attempts to concentrate traces of rare earths by using pptn. and ion-exchange techniques are described and the results tabulated. With EDTA as a complexing agent, 98% of the La present in 1·5 g of Th was co-precipitated with 1% of the Th. By ion exchange both Y and La were concentrated. E. G. CUMMINS

431. **The volumetric determination of plutonium with ethylenediaminetetra-acetic acid.** G. W. C. Milner and J. L. Woodhead (A.E.R.E., Harwell, England). *Analyst*, 1956, **81**, 427–429.—The complexing action of EDTA with plutonium ions was investigated and found to provide a suitable basis for a volumetric method for determining milligram amounts of Pu. Excess of 0·01 *M* EDTA soln. is added to a soln. of Pu in HCl, the pH is adjusted to 2·5 with aq. NH_3, and the excess of EDTA is titrated with 0·01 *M* $Th(NO_3)_4$ soln., the indicator used being a mixture of alizarin red S and methylene blue. Plutonium forms a 1 to 1 complex with EDTA. The error is $< 1\%$ for amounts of $\simeq$ 10 mg. The method is not specific for Pu since Fe, Ti, Th, Ga and probably V form complexes with EDTA at pH 2·5. A. O. JONES

432. **Carbon in non-ferrous metals. I. Methods of determination.** J. Fischer and W. Schmidt (Metallges. A.-G., Frankfurt a. M., Germany). *Z. Erzbergb. Metallhüttenw.*, 1955, **8**, 529–532.—Various methods for determining C in non-ferrous metals are discussed. Oelsen's method of absorbing CO_2, formed by combustion, in $Ba(OH)_2$ soln. followed by electrometric titration was unsuitable, but the modification of Oelsen *et al.* (*Arch. Eisenhüttenw.*, 1951, **22**, 225) and Abresch in which an electrode of MnO_2 was used in place of calomel was satisfactory. The combustion apparatus and gas-purification train are described. The soln. for absorption of CO_2 was made by dissolving 10 g of $BaCl_2.2H_2O$, 5 ml of 96% ethanol and 0·6 ml of 30% H_2O_2 in a litre of H_2O. After absorption is complete, the $Ba(OH)_2$ soln. is titrated with 0·01 *N* HCl or oxalic acid. Details of manipulation and of absorption apparatus are given. The method was applied successfully for determining the low-carbon content of Al, Cu, Zn and Ti and their alloys. CHEM. ABSTR.

433. **Stable carbon isotope analysis by optical spectroscopy.** R. E. Ferguson and H. P. Broida (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1436–1438.—The use of C_2 radiation from acetylene, burned in a small welding torch (burner assembly illustrated, orifice diameter 0·5 mm), for the measurement of relative concn. of the carbon isotopes ^{12}C and ^{13}C is described. Samples of acetylene, enriched with ^{13}C between the levels of 3·6 to 23 atoms-%, were burned with air and the relative emission-intensities of the Swan bands due to the isotopic C_2 radicals were measured photo-electrically. A representative calibration curve of the intensity ratio $^{12}C^{13}C/^{12}C^{12}C$ *vs.* ^{13}C abundance in the fuel is presented and discussed. E. G. CUMMINS

434. **Methods of testing carbon black.** Carbon Black Industry Ctee. (Cabot Carbon Co., Pampa, Tex., U.S.A.). *Bull. A.S.T.M.*, 1956, No. 215, 51–58.—The following tentative standard procedures for testing samples of carbon black are given—pellet-size distribution, solvent-extractable material, water-wash sieve residue, mechanical attrition (of pelleted material), degree of discoloration of benzene, fines content, ash content, loss on heating at 105°, pour density, volatile content (excluding H_2O), pH value and mass strength (cylindrical column of pellets). W. J. BAKER

435. **Chemical analysis with the ultra-violet filter-photometer. III. Determination of traces of cyanide ions.** Takeshi Kato and Koichiro Shinra (Kita College, Osaka Univ., Toyonaka, Osaka). *J.*

Chem. Soc. Japan, Pure Chem. Sect., 1956, **77** (6), 885–888.—Cyanide ions react with the Pd complex of 1-nitroso-2-naphthol (**I**) to yield stable $Pd(CN)_4^{2-}$ and free **I**. The extinction of the latter at pH 10 (375 mμ) is proportional to the amount of CN^- (0·5 to 10 μg per ml). The presence of those metal ions that form stable **I** complexes (*e.g.*, Fe, Pb, Cu, Ni, Co, Ag, Hg) vitiates the estimation. The effect of Cu, Ni and Co is eliminated, however, by the addition of EDTA (disodium salt). Anions such as SO_3^{2-}, NO_2^- or S^{2-} do not interfere with the determination. The mercury arc line at 366 mμ can be used in place of a filter. For the prep. of the Pd complex of **I**, $PdCl_2.2H_2O$ (2 g) is dissolved in dil. HCl (200 ml), treated with 30% H_2O_2 (10 ml), made basic with NaOH and diluted to 3 litres together with 300 ml of acetic acid; **I** soln. (1% in 50% acetic acid, 450 ml) is added, boiled for 20 to 30 min. and filtered; the ppt. is washed with acetic acid and water. The sample soln. (40 ml) is made up to 50 ml with 3 ml of buffer (67 g of NH_4Cl and 500 ml of aq. NH_3 soln. of sp.gr. 0·88 made up to 1 litre) and 20 mg of the Pd complex of **I** is added before measurement of the extinction. K. SAITO

436. **Rapid titrimetric determination of silica in materials containing fluorine.** I. Sajó and L. Barna (Res. Inst. for Iron Industry, Budapest, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 19–25 (in German).—The method previously described (Sajó, *Kohászati Lapok*, 1954, **9**, 400) has been adapted for the determination of silica in fluorine-containing materials such as cryolite. Results are obtained rapidly and agree well with those by gravimetric methods. *Procedure*—For fluorides sol. in water or acids, stir the sample (1 to 2 g) in a plastics beaker for 2 min. with a previously boiled and cooled mixture of HNO_3 (*d*, 1·24) (30 ml) and HCl (*d*, 1·19) (10 ml). For fluorides insol. in acids, fuse the sample (0·1 to 2 g) in a silver dish with KOH, digest with H_2O (< 60 ml), transfer to a plastics beaker, add a previously boiled and cooled mixture of HNO_3 (*d*, 1·4) (10 ml) and HCl (*d*, 1·19) (20 ml), stir with H_2O (10 ml) and add NaF (1 g). For fluorides with a high aluminium content, fuse the sample (0·5 g) in a silver dish with pptd. $CaCO_3$ (0·5 g) and KOH (6 to 8 g) for 6 to 8 min., digest with H_2O (< 60 ml) and continue as for acid-insol. samples. In each of the three cases, complete the analysis as follows—saturate the soln. with KCl, filter under suction, wash the ppt. with a saturated soln. of KCl in 50% aq. ethanol until free from acid, take up the ppt. in hot H_2O and titrate the liberated HF with standard alkali. Subtract a reagent blank. A. R. ROGERS

437. **Fast neutron activation analysis. Silicon and aluminium.** S. E. Turner (Magnolia Petroleum Co., Dallas, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1457–1459.—A Van de Graaf accelerator is used as a source of accelerated deuterons (200 to 300 kV) to strike a zirconium - tritium target (0·75 in. diameter, 1 mg per sq. cm). This provides 14-meV electrons, sufficient to produce the *n*, *p* reaction on Si, giving the 2·4-min. ^{28}Al radioisotope, and the *n*, α reaction on Al, giving the 15-hr. ^{24}Na, both in measurable quantities. The samples, in plastic vials ($^9/_{16}$ in. diameter) are supported directly in front of the target, and the radioactivity is measured in a well-type sodium iodide scintillation crystal counter. The method is accurate to within 5% for samples containing 0·4 g or more of SiO_2 and 0·5 g or more of Al_2O_3. Phosphorus, Pr and Cr interfere with the determination of Si, while Mg and Fe interfere with the determination of Al. E. G. CUMMINS

438. **Detection of germanium with phenylfluorone and the constitution of the complex.** P. Stipanits and F. Hecht (II Chem. Inst., Univ. Vienna). *Z. anal. Chem.*, 1956, **152** (1–3), 185–192.—The complex of Ge with phenylfluorone (**I**) is insol. in org. solvents and accumulates at the interface between water and CCl_4. This permits the detection of 0·02 μg of Ge per ml of soln. The complex contains two mol. of **I** for each atom of Ge. *Procedure*—Dilute the sample (1 ml) to 5 ml with H_2O, acidify with a few drops of conc. H_2SO_4 and add the soln. of **I** (5 drops). Shake with CCl_4 (1 ml) and inspect the interface after 30 min. against a white background. J. P. STERN

439. **Detection of a small amount of germanium by means of an ion-exchange resin. III. Application to minerals.** Takeo Murase and Hidetake Kakihana (Faculty of Sci., Nagoya Univ., Chigusaku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (6), 936–941.—Most metal ions that interfere with the colorimetric detection of Ge with haematoxylin (**I**) adsorbed on an anion-exchange resin are removed by the addition of a cation-exchange resin to the sample drop. When their concn. is high (> 1000 times the weight of the Ge), the use of Amberlite IR-120 (H) in 0·5 *N* HCl is recommended. The resin containing **I** (Kakihana *et al.*, *Ibid.*, 1954, **75**, 907; *Anal. Abstr.*, 1955, **2**, 2069) is then added to the acid soln. and the granules are transferred into 0·1 *N* HCl for the colour change to be observed. The limit of detection is ≃ 0·25 μg of Ge in the presence of 7·5 mg of other ions. In the presence of Sn or Sb (> 10^4 times the wt. of the Ge), $GeCl_4$ is distilled on a micro scale instead of being treated with IR-120. Minerals (10 to 20 mg) are decomposed with HNO_3 and HCl and submitted to either of these procedures. K. SAITO

440. **Determination of germanium in low concentrations.** M. Senegačnik and L. Kosta. *J. Stefan Inst.* (*Ljubljana*) *Rep.*, 1955, **2**, 15–19 (in English).—In a comparison of methods for the determination of Ge in low concn. the distillation method proved to be faster than the extraction method for single determinations, but for routine work the extraction method requires simpler equipment and makes better use of the time. For the distillation method for the determination of Ge in a zinc concentrate, place 0·2 to 0·5 g of sample in a porcelain crucible in an electric furnace and roast at 650° for 1 hr. and at 800° to 900° for 20 to 30 min. Transfer the cold sample to a distilling flask and add $HClO_4$ (1:1). After rinsing with H_2O, neutralise the contents of the flask and dilute to 25 ml. Add an equal vol. of conc. HCl before distilling into 15 ml of H_2O. To 12·5 ml of the distillate add 1 ml of gum arabic soln. and 7·5 ml of phenylfluorone soln. and dilute to 25 ml; set aside for 30 min. at 20° and measure the extinction against a blank. For the extraction method, transfer the zinc concentrate to a separating funnel and remove the particles in the crucible with a little $HClO_4$ and H_2O. Add four times as much conc. HCl and stopper the funnel. After 1 hr. with moderate shaking add 10 to 15 ml of CCl_4 and shake vigorously for 2 to 3 min. After the separation of phases, run off the CCl_4 into another funnel and repeat the extraction with 10 ml of CCl_4. Add a little conc. HCl to the combined extractions. Transfer the CCl_4 to another separating

funnel containing 15 ml of H_2O and, after stoppering, shake vigorously for 2 to 3 min. Run off the H_2O layer into a 25-ml volumetric flask and dilute to the mark. Add conc. HCl to an aliquot and measure the extinction against a blank after 30 min. CHEM. ABSTR.

441. **Determination of a small amount of germanium in lignite and coal.** Hiroshi Nishida (Ind. Training Inst. of Iwate Prefecture, Uchimaru, Morioka). *Japan Analyst*, 1956, **5** (7), 389–392.—When lignite or coal is decomposed with H_2SO_4 and HNO_3, a significant amount of Ge becomes so firmly adsorbed by the silica that some remains adsorbed on the distillation of $GeCl_4$. The ash must therefore be treated with HF and H_2SO_4 before the distillation; Ge in the distillate is colorimetrically determined by Cluley's method (*Analyst*, 1951, **76**, 523). *Procedure*—The sample (100 mesh, 1 g) is decomposed by conc. H_2SO_4 (10 ml) with addition of HNO_3 (sp. gr. 1·40) in 2 to 3-ml portions, diluted to 20 to 30 ml and filtered. The residue is ignited, treated with H_2SO_4 (1 ml), HF and HNO_3, diluted and combined with the filtrate. This soln. is mixed with HCl (1 + 1, 120 ml) and $GeCl_4$ is distilled; a portion of the distillate is submitted to photometry with phenylfluorone. K. SAITO

442. **Micro-determination of arsenic and antimony in metallic germanium and germanium oxide.** Hidehiro Gotô and Yachiyo Kakita (Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 739–742.—Colorimetric determination of As (> 0·1 p.p.m.) with molybdate and of Sb (> 0·01 p.p.m.) with methyl violet (**I**) (Gotô *et al.*, *Ibid.*, 1952, **73**, 339) was applied to the analysis of pure Ge. Separation of As from Ge, P and Si is satisfactorily achieved by extracting its diethyldithiocarbamate (**II**) with CCl_4 from an acid soln. The organic layer is treated with H_2SO_4 and HNO_3 and submitted to colorimetry with $(NH_4)_2MoO_4$ and hydrazine sulphate. Antimony is co-pptd. with MnO_2, dissolved in H_2SO_4, oxidised with Ce^{4+}, mixed with **I** soln. and extracted with amyl acetate. *Procedure*—For As, the sample (1 g) is dissolved in H_2O_2 (30 per cent., 2 + 1, 60 ml); the GeO_2 is dissolved in NaOH (3 *N*, 10 ml), made acid with 6 *N* HCl (10 ml), diluted to ≃ 25 ml and treated with KI (10%, 3 ml) and Na_2SO_3 (1 g) at 50°. The product is mixed with 0·1% **II** soln. (3 ml) and extracted with CCl_4 (2 × 5 ml). The organic layer is heated to white fumes with 6 *N* H_2SO_4 and conc. HNO_3 (2 ml), oxidised with 0·01 *N* $KMnO_4$ (2 to 3 drops) and made up to 20 ml together with 1% $(NH_4)_2MnO_4$ and 1% hydrazine sulphate (in a boiling-water bath) for the extinction to be measured at 850 mμ. For Sb, a soln. of the sample in NaOH soln. is similarly prepared and made up to ≃ 50 ml together with 6 *N* H_2SO_4 (7 ml). The acid soln. is boiled with 0·5% $MnSO_4$ (2 ml) and 0·5% $KMnO_4$ (2 ml). The pptd. MnO_2 is filtered off, dissolved in *N* H_2SO_4 (≃ 10 ml) containing a few drops of H_2O_2, heated to white fumes and dissolved in 6 *N* HCl (3 ml). This soln. is oxidised with $Ce(SO_4)_2$ (2% in *N* H_2SO_4, 0·3 ml), and treated with hydrazine sulphate soln. (1%, 5 ml) (to decompose the excess of Ce^{4+}), aq. **I** soln. (0·1%, 1 ml) and Na citrate (30%) until the colour turns green (total vol. ≃ 25 ml). This is extracted with amyl acetate (5 ml) for 1 min., and the extinction is measured at 600 mμ. K. SAITO

443. **Fluorimetric determination of tin.** J. R. A. Anderson and S. L. Lowy (Univ. of Technol., Sydney, N.S.W., Australia). *Anal. Chim. Acta*, 1956, **15** (3), 246–253.—Optimum conditions have been established for the micro-determination of Sn by utilising the blue fluorescence developed in a slightly alkaline soln. containing Sn^{2+} and 6-nitro-2-naphthylamine-8-sulphonic acid. Since many cations, *e.g.*, UO_2^{2+}, VO^{2+}, Fe^{2+} and Ti^{3+}, produce fluorescence or part-quenching of the fluorescence due to Sn^{2+}, the Sn^{2+} must be separated initially. The reduction to Sn^{2+} is effected with hypophosphorous acid in the presence of a small amount of $HgCl_2$; tartaric acid serves to keep the Sn in soln. The reduction and the development of fluorescence are conducted in an atm. of CO_2. *Procedure* (*for Cu - Sn alloys*)—Dissolve the sample (≡ ≃ 10 mg of Sn) in conc. HNO_3, and after removing the ppt. of metastannic acid by centrifuging dissolve it in 10 ml of 5 *N* HCl containing 1 g of tartaric acid, warming until the soln. is clear. Cool, add 1 ml each of saturated aq. $HgCl_2$ soln. and 30% hypophosphorous acid, heat gently until the ppt. coagulates, add 30 ml of aq. 5 *N* NH_3, followed (when cool) by 10 ml of a 0·1% (w/v) aq. soln. of the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid. When max. fluorescence has developed (after ≃ 2 hr.) make the soln. up to 1 litre with H_2O, and then measure the fluorescence of an aliquot (10 ml) made up to 100 ml with H_2O and 10 ml of aq. 5 *N* NH_3. The measurement is made in a photo-electric photometer with fluorescent attachment, with an 18-ml cell and filters to absorb the exciting radiation (365 mμ). The content of Sn is calculated from the linear calibration curve for freshly prepared standard soln. of Sn. The accuracy is high. W. J. BAKER

444. **Combined electro-chemical method for determining tin and antimony.** K. N. Bagdasarov. *Soobshch. Nauch. Rabotakh Chlenov. Vses. Khim. o-va. im. Mendeleeva*, 1955, (1), 15–17; *Ref. Zhur., Khim.*, 1956, Abstr. No. 10,091.—Small quantities of Sb and Sn (> 3 mg per litre) in the presence of large quantities of Zn (≃ 100 g per litre) are pptd. on a copper-coated platinum cathode at potentials of −0·650 V and from 0·850 to 0·950 V, respectively (vol. of soln. 100 to 1000 ml, pH 1·5, temp. 100°). To prevent corrosive action of Cl, 1% of hydroxylamine hydrochloride is added to the electrolyte. The period of electrolysis is 2 hr. and the accuracy is within ± 5%. In the presence of larger amounts of Sn, the deposit, after the electrolysis is completed, is dissolved in 10 ml of H_2SO_4 (1:2) until the red copper coating appears; the soln. is treated with 0·5 g of hydroxylamine hydrochloride and 3 drops of gelatin soln.; it is then diluted to 25 ml and polarographed. Up to 0·05 mole per litre of Al^{3+}, Ni^{2+}, Cr^{3+} and Zn^{2+} does not interfere. The same results are obtained on a nickel-coated platinum electrode at pH 2·0. If pptn. is carried out on a nichrome electrode at pH 2 to 2·5, the deposit, containing 3 to 5 mg of Sb and Sn, is dissolved in a mixture of H_2SO_4 (2 ml) and HCl (5 ml). Hydrogen peroxide (2 to 3 drops) is added to prevent displacement of tin by nickel, the excess of H_2O_2 is removed by adding hydroxylamine hydrochloride and the resulting solution is polarographed. In determining Sb and Sn in the presence of Pb, the Pb is pptd. by H_2SO_4, and filtered off, and HCl to bring the pH to 1·5 is added to the filtrate. The electrolysis of Sn and Sb is then carried out in a boiling soln. at a potential of 1·2 V and the determination completed polarographically. R. LORD

445. **Effect of iron on determination of tin in brass and bronze. Application of radio-isotope techniques.** C. N. La Rosa, I. Geld, A. Ticker, S. F. Di Lauro and J. L. Kalinsky (New York Naval Shipyard, Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1447–1451.—An investigation of the sources of error in the estimation of Sn, pptd. as metastannic acid, in brass and bronze is reported. Detailed data of the partially compensating errors of co-pptn. and solubility are tabulated and graphs are given for two different digestion temp. Under routine conditions, digestion at temp. below boiling point involves the least error for samples containing 7·85% of Sn, and the same error as digestion at boiling point for samples containing 4·41 and 0·97% of Sn. The relationship between iron content and iron co-pptd. with metastannic acid is discussed and the co-pptn. of iron is shown to follow Freundlich's adsorption isotherm. E. G. CUMMINS

446. **Visual titrations with diethyldithiocarbamate. III. Determination of lead.** R. Wickbold (Chem.-Werke Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **152** (4), 266–270.—Diethyldithiocarbamate (**I**) displaces dithizone (**II**) from the red Pb - **II** complex at pH values below 6. The products are the colourless Pb - **I** complex and green **II**, and all these substances are sol. in chloroform. **II** is thus a useful indicator for the visual titration of Pb with **I** between pH 5 and 6. Metals forming less sol. complexes with **I** (Hg, Ag, Cu, Ni and Co) and metals forming complexes with **II** (Bi, Cd, Tl and Zn) interfere; Sn and Sb do not interfere. The method is accurate to within ±1% on 0·5 to 1·5 mg of Pb and to within ± 0·3% on 3 to 500 mg of Pb, and is useful in the analysis of soft metals and of PbO_2 produced during electrolysis. *Procedure*—To the sample add 10% aq. tartaric acid (10 ml) and dilute to 100 ml. Adjust the pH with aq. NH_3 and HCl until litmus turns red, then add Na acetate - acetic acid buffer soln. (136 g and 26 g, respectively, per litre) (10 ml) and a chloroform soln. of **II** (5 mg per litre) (5 ml). Shake the mixture continuously and titrate with 0·1 or 0·01 *N* **I** to a pure green end-point. Near the end-point add **I** dropwise and shake for several seconds to permit complex exchange. J. P. STERN

447. **Visual titrations with diethyldithiocarbamate. VI. A further method for the estimation of lead.** R. Wickbold (Chem. Werke Hüls A.-G., Marl, Krs. Recklinghausen, Germany). *Z. anal. Chem.*, 1956, **153** (1), 21–23.—A fairly large number of heavy metals interfere in the direct titration of lead with diethyldithiocarbamate (*cf. Anal. Abstr.*, 1957, **4**, 446). In the following procedure, the method already described for the determination of Cd (*cf. Anal. Abstr.*, 1957, **4**, 409) is applied to the determination of Pb. *Procedure*—The sample (> 50 mg) should be contained in a vol. of < 100 ml. After the addition of 25 ml of tartaric acid soln. (10%), the soln. is made alkaline to phenolphthalein with NaOH soln. (10%), and a further 5 ml is added in excess. Following the addition of 10 ml of KCN soln. (20%), the Pb is pptd. with 10 ml of ≃ 0·1 *N* Na diethyldithiocarbamate soln. The soln. is well shaken, and after 5 to 10 min. the ppt. is extracted with $CHCl_3$ (3 × 25 ml, and 1 × 10 ml). The organic layer is thoroughly shaken with 50 ml of H_2O and 10 drops of aq. NH_3 (25%), and after separation this aq. extract is re-extracted with 10 ml of $CHCl_3$. The organic layers are combined, 10 ml of a buffer soln. (pH 5) and 5 ml of 0·01 *N* $CuSO_4$ soln. are added, and the whole is shaken. The colourless Pb diethyldithiocarbamate is converted into the yellow to brown copper complex. Without further separation, standard $HgCl_2$ soln. (0·001 *N* for 0·2 to 5 mg of Pb, 0·01 *N* for 5 to 50 mg of Pb) is added in portions with strong shaking until the $CHCl_3$ layer becomes colourless with the formation of Hg diethyldithiocarbamate. J. H. WATON

448. **Micro-electrolytic determination of lead and its application to the analysis of tin-base and lead-base alloys.** C. Cimerman and M. Ariel (Israel Inst. Technol., Haifa, Israel). *Anal. Chim. Acta*, 1956, **15** (3), 207–212.—From 2 to 10 mg of Pb can be determined by electro-deposition at 80° as PbO_2 on the platinum anode of the Clarke - Hermance micro-electrolytic cell (*cf. Brit. Abstr. A*, 1932, 492). Cathodic deposition of Pb is prevented by keeping the concn. of HNO_3 in the cell at ≃ 15% v/v and adding aq. $Cu(NO_3)_2$ soln. (≡ 1 mg of Cu); 30 to 50 mg of urea should also be present to remove any HNO_2. The PbO_2 deposit is dried at 120° and weighed. This procedure is applicable to alloys of Sn and Pb containing Sb and Cu provided that the Pb (together with Cu) is separated initially by pptn. with sodium sulphide, and the well-washed ppt. is then dissolved in 2 ml of warm HNO_3 (1 + 3). The max. error is ≃ 0·6%. W. J. BAKER

449. **Precipitation of lead chromate from homogeneous solution.** W. A. Hoffman and W. W. Brandt (Purdue Univ., West Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1487–1489.—A modification of the standard procedure for lead and chromium determination may be represented as—

$$2Cr^{3+} + BrO_3^- + 5H_2O \rightarrow CrO_4^{2-} + Br^- + 10H^+$$
$$5Br^- + BrO_3^- + 6H^+ \rightarrow Br_2 + 3H_2O.$$

The chromium is slowly oxidised to chromate by bromate, giving large pure lead chromate crystals. E. G. CUMMINS

450. **Determination of titanium by cupferron with Complexone III as the masking agent.** A. K. Majumdar and J. B. R. Chowdhury (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1956, **15** (2), 105–108.—By pptn. with cupferron in the presence of EDTA, Ti is separated from AsO_3^{3-}, BO_3^{3-}, MoO_4^{2-}, VO_4^{3-}, WO_4^{2-}, AsO_4^{3-}, alkaline earths and alkali metals, Mg, Pb, Cu^{II}, Bi, Cd, Zn, Mn^{II}, Ni, Co^{II}, Sb^{III}, Fe^{III}, Al, Cr^{III}, Zr^{IV}, Th^{IV} and the rare earths, but U^{IV}, U^{VI}, Sn^{II}, Sn^{IV} and Be are co-pptd; PO_4^{3-} also interfere. *Procedure*—To the acid soln., containing Ti^{IV} and other metals, add sufficient EDTA (disodium salt) to retain all the metals in soln. Add aq. ammonium acetate until the soln. is yellow to methyl orange, dilute to ≃ 350 ml, cool to 10° and add slowly, with stirring, a 6% aq. soln. of cupferron until the Ti is pptd. Filter, wash with cold water containing a little cupferron, dry, ignite to TiO_2 and weigh. Separation from WO_4^{2-} or Sb^{III} can be effected by pptn. from a soln. containing tartaric acid and made alkaline to methyl orange with ammonium acetate. In the presence of EDTA, Ti can be pptd. quant. with cupferron in the pH range 4·3 to 7·0. W. C. JOHNSON

451. **Polarography of titanium in strong mineral acid media.** J. J. Lingane and J. H. Kennedy (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (3), 294–300.—The polarographic behaviour of the Ti^{4+} - Ti^{3+} couple at 25° in 1 to 15 *M* aq. soln. of HCl, $HClO_4$, H_2SO_4 or

H_3PO_4 is reported. In 4 to 15 *M* H_2SO_4 the reversible formal potential becomes more positive than the potential of H^+ reduction on Pt, so that such soln. can be used for coulometric titrations with electrolytically generated Ti^{3+} at the platinum cathode. Although Ti^{4+} can be determined from the cathodic diffusion current in 3 to 6 *M* HCl, accurate measurements of the anodic diffusion current, for the determination of Ti^{3+}, are not possible. In 1 to 15 *M* H_3PO_4 the Ti^{4+} - Ti^{3+} couple is completely reversible, the cathodic and anodic waves are both sharply defined, and the values of $E_{\frac{1}{2}}$ (−0·25 to −0·09 V *vs.* the S.C.E.) enable Ti to be determined in the presence of its associated elements. Although the characteristics of the polarographic waves in these strongly acid media are well suited to the determination of Ti, it is recommended that such measurements should be made in H_3PO_4 soln., especially when the usual complexing agents are inapplicable or undesirable.
W. J. BAKER

452. **Determination of carbon in titanium and titanium alloys by combustion.** M. Codell, G. Norwitz and E. F. Schneider (Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (3), 218–222.—In the apparatus and procedure described, the sample (1 to 5 g) is burnt in a stream of O in a ceramic boat insulated from the quartz reaction tube of the furnace. Complete oxidation of C is attained by covering the sample with granulated Pb as a flux and placing it in the furnace at an initial temp. of 900° to form a Pb - Ti alloy before oxidation to PbO_2 occurs at higher temp. The evolved gases are passed through MnO_2, $CuSO_4$ and Anhydrone to remove SO_2, Cl and H_2O. Pure O must be used. The standard deviation is $\simeq \pm$ 0·008% (10 analyses of a sample with 0·284% of C). W. J. BAKER

453. **A new highly selective method for the photometric determination of zirconium.** H. Flaschka and M. Y. Farah (National Research Council, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 1956, **152** (6), 401–411.—The intense colour given by Zr with catechol violet in the presence of EDTA (*cf. Anal. Abstr.*, 1956, **3**, 2688) is the basis of a highly selective absorptiometric method for the determination of small quantities (< 60 μg) of Zr. Oxidising agents, complex-forming anions, Sb^{III}, Sn^{IV} and Hg^{I} interfere and must be absent; U, Y, Ti, Cr and Th interfere if present in 100-fold excess; other metallic metals are without effect even if present in 3000-fold excess. *Procedure*—Add 0·1 *M* EDTA (3 ml) to the sample soln., adjust to pH 5·2, add 0·001 *M* aq. catechol violet (2·00 ml), dilute to 25 ml with acetate buffer of pH 5·2 and mix. After 30 min., compare the extinction at 620 mμ with that of a blank soln. prepared similarly but with the addition of 1% ammonium fluoride (one drop).
A. R. ROGERS

454. **A new reagent for the determination of thorium.** M. R. Verma, K. C. Agrawal and S. D. Paul (Nat. Phys. Lab. of India, New Delhi). *Nature*, 1956, **178**, 324.—*m*-Nitrocinnamic acid will satisfactorily separate Th from other tervalent rare earths. A granular ppt. of the tetra(nitrocinnamate) is formed, which can be weighed as such, without the usual ignition to ThO_2. *Procedure*—Add an alcoholic soln. of *m*-nitrocinnamic acid to a soln. of the thorium salt at pH ≯ 2·0, then adjust to a pH of 3·8 to 4·0. Filter off the ppt., wash it with hot alcohol and weigh. For mixtures of rare earths containing only a small proportion of Th, a double pptn. is necessary. Interference is caused by Ti^{4+}, Zr^{4+}, Ce^{4+} and other quadrivalent ions.
G. S. ROBERTS

455. **Spectrophotometric study of the thorium - morin mixed-colour system.** M. H. Fletcher and R. G. Milkey (U.S. Geological Survey, Washington, D.C.). *Anal. Chem.*, 1956, **28** (9), 1402–1407.—At pH 2, one thorium ion reacts with 2 molecules of morin, the reaction having an equilibrium constant of 1×10^6. The complex is critically examined as a basis for the spectrophotometric determination of Th^{4+}. The aqueous solution at the abs. max. of 410 mμ obeys the Beer - Lambert law and is sensitive with respect to Th^{4+}. The effects of pH, ethanol and morin concn., time of prep., temperature, age of morin reagent, the serious interference of Zr^{4+}, Al^{3+} and Fe^{3+}, the minor interference of Fe^{2+}, Yb^{3+}, Y^{3+}, UO_2^{2+}, Pr^{3+} and Pb^{2+}, and the virtual non-interference of La^{3+} and Ca^{2+} are discussed. A method of determination of Th^{4+} in pure solutions is deduced. D. A. PANTONY

456. **EDTA titration of thorium in gas mantles and in glasses with catechol violet as indicator.** M. Malát, J. Pelikan and V. Suk (Dept. Anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Chemist Analyst*, 1956, **45** (3), 61–62.—Procedures are described for the estimation of thorium (in gas mantles) as nitrate in the presence of Ce, Be, Al and Mg, and in the presence of Ba, Be, La, Al, As and Sb (in optical glasses). In the former case the mantle is digested with conc. HNO_3 and then diluted with water before titration, and in the latter case the pulverised glass is digested with $HClO_4$ and again diluted before titration. The pH of the soln. is adjusted to between 3 and 3·5 and, after the addition of 5 to 8 drops of catechol violet soln. (0·1% in water), the soln. is titrated with EDTA until the reddish-purple colour changes to lemon-yellow. The accuracy of the method is within ±1·5%. C. A. SLATER

457. **Anion-exchange studies. XXI. Th^{IV} and U^{IV} in hydrochloric acid. Separation of thorium, protactinium and uranium.** K. A. Kraus, G. E. Moore and F. Nelson (Oak Ridge Nat. Lab., Tennessee, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 2692–2695.—The behaviour of Th^{IV} and U^{IV} in HCl soln. has been investigated by using a strong base quaternary amine resin (Dowex-1, about 200 mesh, approx. 10% DVB). Quadrivalent Th shows no absorption in HCl concn. of 0·1 to 12 *M*; U^{IV} shows little absorption at concn. below 5·5 *M* HCl, but the absorption rapidly increases in higher concn. The absorption behaviour of these elements is compared with that of others of the same valency. A method is described for the separation of Th^{IV}, Pa^{V} and U^{VI}, as well as for the separation of U^{IV} and U^{VI}, which makes use of the different degrees of absorption of these elements in HCl soln.
C. A. SLATER

458. **Determination of phosphorus by precipitation as oxine molybdophosphate.** J. A. Brabson and O. W. Edwards (Tennessee Valley Authority, Wilson Dam, Ala., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1485–1487.—A study of the gravimetric determination of P as the oxine salt of molybdophosphoric acid (*cf.* Scharrer, *Biochem. Z.*, 1933, **261**, 444) is described. E. G. CUMMINS

459. **Analytical chemistry of quinquevalent phosphorus. IV. Determination of pyrophosphoric acid.** J. Fischer and G. Kraft (Inst. anorg. Chem.,

Goethe Univ., Frankfurt, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 56–76.—The literature is surveyed and known methods of determining pyrophosphate are examined in detail, particularly direct alkalimetric titration, pptn. of $Ca_2P_2O_7$ and simultaneous titration of acid liberated thereby, and pptn. of $Zn_2P_2O_7$ and simultaneous titration of liberated acid. All soln. must be kept free from CO_2. (*i*) For direct alkalimetry, acidify the soln. containing 70 mg of $P_2O_7^{4-}$ in 60 ml beyond the stage of $H_2P_2O_7^{2-}$. Remove CO_2, stir, and titrate with 0·1 *N* NaOH. Determine the end-point electrometrically (glass electrode). Calculate the content of $P_2O_7^{4-}$ from the difference in consumption of NaOH between the quaternary and secondary point of equivalence. This procedure gives high results in the presence of condensed phosphates and is inaccurate in the presence of PO_4^{3-}, giving a flatter titration curve. (*ii*) For titration after formation of $Ca_2P_2O_7$, neutralise the soln. (70 to 100 mg of $P_2O_7^{4-}$ in 60 ml) exactly to the $H_2P_2O_7^{2-}$ stage. Then titrate (with a glass electrode as indicator) with 0·1 *N* NaOH to pH 7 and add 1 ml of neutral saturated $CaCl_2$ soln. Complete the titration (without filtration) adding 2 drops of NaOH at a time. Alternatively, use dimethyl yellow (change from red to yellow) as indicator for the neutralisation to $H_2P_2O_7^{2-}$ and phenolphthalein for the addition of Ca, as colour indicators. This procedure is accurate to within ± 0·5% on 60 to 100 mg, but in the presence of the lower-mol.-wt. polyphosphates it gives high results. Metaphosphates do not interfere. (*iii*) Titration after pptn. of $Zn_2P_2O_7$ is the most useful procedure. Adjust the soln. (150 mg of $P_2O_7^{4-}$ in 50 ml) to pH 3·8 (glass or quinhydrone electrode) and add neutral 33% $Zn(NO_3)_2.6H_2O$ soln. (20 ml). After 3 min., back-titrate the acid liberated to pH 3·8 with 0·1 *N* NaOH. Preferably use a slight excess of NaOH and determine this excess after 30 min. when equilibrium is attained. The accuracy is within ± 0·5%. Ortho- and tripoly-phosphate interfere, but metaphosphate does not. J. P. STERN

460. **Gradient elution chromatography of phosphates.** J. A. Grande and J. Beukenkamp (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1497–1498.—The resolution of five phosphates from a mixture is described. One standard KCl solution is employed in the apparatus illustrated, buffered with acetate at pH 5·0.
E. G. CUMMINS

461. **The analytical determination of ortho- and pyro-phosphates in copper-plating solutions.** S. M. Gorelik. *Trudy Gos. Nauch. Inst. Khim. Prom.*, 1955, **2**, 66–74; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,571.—It is possible to use the gravimetric magnesia mixture method or the colorimetric molybdophosphate method for the separate determination of pyro-(**I**) and ortho-phosphates (**II**) in copper-plating soln. By using the property of **I** whereby it is completely converted into **II** on being boiled with strong acid, determine **II** first, and then total phosphates after boiling. Experiments both on the pure salts and in soln. containing $CuSO_4.5H_2O$ (in concn. as used in industry) show that both methods of analysis give an accuracy sufficient for process control. The colorimetric method is recommended for rapid determinations, the time required being 15 to 20 min. C. D. KOPKIN

462. **Titrations with alkaline permanganate in the presence of tellurate: determination of phosphite, arsenite, sulphite, thiosulphate and antimonite.** I. M. Issa and R. M. Issa (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (3), 62–65.—*Procedure*—To $KMnO_4$ soln. (25 ml; 0·1 or 0·01 *N*) in a beaker are added telluric acid (0·2 g) and sufficient 5 *N* NaOH to make the soln. 0·1 to 5 *N*. The soln. is stirred and the reductant (5 ml; approx. 0·1 or 0·01 *N* soln.) is added. After 3 to 5 min. for AsO_3^{3-}, SO_3^{2-}, SbO_3^{3-} and $S_2O_3^{2-}$, and 15 min. for PO_3^{3-}, the soln. is poured into an ice-cold soln. of ferrous ammonium sulphate (50 ml; 0·1 or 0·01 *N*) and made 3 *N* in acid with 6 *N* H_2SO_4. The excess of Fe^{2+} is titrated with standard $KMnO_4$ soln. after adding H_3PO_4. The method is accurate to within ± 1·0%. C. A. SLATER

463. **Separation of arsenic, antimony and tin by anion exchange.** R. Klement and A. Kühn (Inst. für anorg. u. anal. Chem., Phil.-Theol. Hochsch., Regensburg, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 146–153.—Separation of As^V, Sb^V and Sn^{IV} as thioarsenate, thioantimonate and thiostannate is achieved by anion exchange on a Dowex-2 column (OH form) and elution with KOH, when 0·5 *N*, 1·2 to 2·5 *N*, and 3·5 *N* KOH, respectively, elute Sn, As and Sb. The accuracy on mixtures containing 50 to 100 mg of Sn and As, Sn and Sb, and As and Sb is generally within ± 1%. Other separations with anions of thio compounds, *e.g.*, Ge from As or from Sb, are briefly mentioned. The separation of As and Sb in the absence of Sn is easier as arsenate and antimonate: on passage through an Amberlite IRA-400 column (SO_4^{2-} form), As only is retained from very dil. KOH while Sb passes through. The As is later eluted with 8% aq. KOH. J. P. STERN

464. **Potentiometric micro-determination of antimony by alkaline permanganate.** I. M. Issa and I. M. El Sherif (Fac. Sci., Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (3), 78.—A soln. of Sb^{3+} (0·5 to 10 ml; ≃ 0·0001 *N*) is made 0·1 *N* in NaOH, and telluric acid (0·1 g) is added. The soln. is titrated with 0·0002 *N* $KMnO_4$ added in 0·05-ml increments, the potentiometer being read after each addition. The potentiometer reading is plotted against vol. of $KMnO_4$ soln. As little as 3 μg of Sb can be titrated with an error of less than ± 5%. C. A. SLATER

465. **A new method for the bromatometric determination of antimony in lead- and tin-base alloys.** D. A. Detmar and W. van der Velde (Inst. Anal. Res. T.N.O., Rijswijk, Netherlands). *Anal. Chim. Acta*, 1956, **15** (2), 173–180.—The sample of alloy (0·5 to 1 g) is dissolved in 25 ml of a soln. of 10 ml of Br in 100 ml of conc. HCl (sp. gr. 1·19); the soln. is boiled to a vol. of < 20 ml, 100 ml of 2 *N* HCl is added and the soln. is again boiled. The Sb^V is now reduced, together with any Cu^{II}, by the addition of 0·1 *M* $TiCl_3$ to the hot soln. until a platinum electrode immersed in it shows a potential of ≃ −50 mV *vs.* the S.C.E. The titration of the Sb^{III} with $KBrO_3$ is subject to interference from the Ti^{III} and Cu^I that are present, although the potentiometric curve shows distinctive end-points; these metals are next oxidised therefore with a 0·1 *M* soln. of $NaVO_3$ in 2 *N* HCl, which has a negligible effect on the Sb^{III}. The 0·1 *M* $NaVO_3$ is added dropwise at room temp. until 1 drop produces a potential jump of 50 to 100 mV at ≃ 400 mV *vs.* the S.C.E. The Sb^{III} is then titrated potentiometrically with 0·1 *N* or 0·02 *N* $KBrO_3$. The method can be used for alloys that contain Pb, Sn, Cu, Bi and As, but Fe interferes when present in appreciable amount. W. C. JOHNSON

466. **Compleximetric determination of bismuth.** G. Rády and L. Erdey (Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1956, **152** (4), 253–258.—Bismuth is determined by titration between pH 1 and 3 with EDTA (disodium salt) in the presence of disodium 1-(*o*-arsonophenylazo)naphth-2-ol-3;6-disulphonate (thoron) (**I**) (Kuznetsov, *Zhur. Obshch. Khim., SSSR*, 1940, **10**, 1512) as indicator. The method is accurate to within ± 0·8% on 3 to 230 mg of Bi. Interference by Th, Ce^{4+}, Zr, La, U^{4+} and Fe^{3+}, and by Cl^-, SO_4^{2-}, F^- and PO_4^{3-} is encountered, that by Fe^{3+} being avoided by reduction with ascorbic acid. *Procedure*—Dilute the soln. of Bi in 0·5 *N* HNO_3 to 60 ml and add 0·5% aq. **I** (2 drops). Titrate the red soln. with 0·05 *M* EDTA to a pure yellow end-point. J. P. Stern

467. **The iodimetric micro-determination of vanadium.** I. Pais (Inst. Inorg. and Anal. Chem., Eötvös Loránd Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 252.—Acidify the soln. containing V^V to pH 2 with H_3PO_4 under an atmosphere of CO_2. Add mannitol and KI and back-titrate the iodine with thiosulphate. For 10 to 50 μg, the accuracy is within 1·5%.

A. G. Peto

468. **The spectrophotometric determination of vanadium as thiocyanate in acetone - water medium.** H. I. Feinstein (U.S. Geological Survey, Washington, D.C., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (2), 141–144.—The blue colour of VO^{2+} is intensified 4 to 5 times by the combined effect of acetone and SCN^-. The reaction is not as sensitive as the peroxide reaction for V but provides a method for the determination of 5 to 15-mg quantities of V. *Procedure*—To the soln. of V (5 ml), containing 0·1 ml of free H_2SO_4, add 1 ml of aq. H_2SO_3 (6%), 15 ml of acetone and 3 ml of 8·33 *M* NH_4SCN, and mix after each addition. Dilute with water to 25 ml and determine the extinction at 750 mμ in a 1-cm cell. Interpret the readings by reference to a graph prepared with known quantities of V.

W. C. Johnson

469. **Spectrophotometric determination of small quantities of vanadium with diphenylbenzidine.** J. Eeckhout and A. Weynants (Univ. of Ghent, Belgium). *Anal. Chim. Acta*, 1956, **15** (2), 145–153.—Dilute solutions of V^V yield a yellow colour with diphenylbenzidine. Factors that affect the development of this colour have been investigated and a method has been evolved for the determination of V in steel. Since most other elements commonly encountered in steel analysis interfere when present in quantities ten times that of the V, they are first separated by electrolysis. *Procedure*—Dissolve the sample of steel (0·1 to 0·5 g) in a suitable acid and evaporate to fumes with H_2SO_4. Dissolve the residue in 50 ml of water and electrolyse with a mercury cathode at 8 to 10 V until the soln. is colourless. Separate from the mercury, neutralise with aq. NH_3 and dilute to 100 ml. To an aliquot containing 0·1 to 1 mg of V add a few drops of 0·01 *N* $KMnO_4$ and, after a few minutes, boil to decomp. the $KMnO_4$; add 50 ml of acetic acid and dilute with water to 100 ml. Add 1 ml of this soln. to 10 ml of a freshly prepared 0·01% soln. of diphenylbenzidine in acetic acid, shake the soln. for 2 min., set aside for 5 to 40 min. (the longer time for the lower concn. of V) and determine the extinction in a 1-cm cell at 480 mμ, in comparison with a blank containing 10 ml of the reagent soln. and 1 ml of dil. acetic acid (1 + 1). Interpret the results by means of a calibration graph. The colour may be developed more rapidly by heating at 50° for 10 min. When the content of V is < 0·05% a greater sample is taken and the V is first separated from the greater part of the Fe and Mn by pptn. with $NaHCO_3$.

W. C. Johnson

470. **A study of the conditions for the formation of niobium thiocyanate. [Determination of niobium in stainless steel.]** A. Bacon and G. W. C. Milner (U.K. Atomic Energy Authority, Harwell, England). *Anal. Chim. Acta*, 1956, **15** (2), 129–140.—The factors that influence the formation and the stability of the thiocyanate complex of Nb in dil. soln. have been investigated and the following conditions have been found to be the most favourable. *Procedure*—Mix 147 ml of conc. HCl (sp. gr. 1·18) with 58·8 ml of water and dilute to 500 ml with acetone. To 34 ml of this mixture add 5 ml of the soln. of Nb containing up to 2 μg of Nb per ml and 0·05 *M* with respect to tartaric acid; add 0·5 ml of 2 *M* $SnCl_2$ in conc. HCl and 9 ml of 6 *M* NH_4SCN; dilute to 50 ml at 23°. Measure the extinction at 385 mμ in a 1-cm cell with the temp. controlled at 23°. No interference results from the presence of Fe or Cr, but the following elements interfere increasingly in the order Ta, U, Mo, W, V and Ti. In the analysis of stainless steel, Nb is only partially dissolved when the sample is treated with dil. H_2SO_4 (1 + 4). After the addition of cupferron the whole of the Nb (+ Ti) is separated by filtration; W and Mo are removed by washing with dil. aq. NH_3 (1 + 19). The residue is dried, ignited, heated with dil. H_2SO_4 and conc. HF to remove SiO_2, and fused with $KHSO_4$; the cooled melt is extracted with 50 ml of 0·5 *M* tartaric acid. The extract is diluted with water to 500 ml and a 5-ml aliquot is taken for the determination of Nb. When the Ti to Nb ratio is low, a correction can be applied (1% of Ti ≡ ≃ 1·2% of Nb), but when the ratio is high, a separation is necessary.

W. C. Johnson

471. **The isolation and determination of protactinium-233.** A. J. Fudge and J. L. Woodhead (A.E.R.E., Harwell, Berks., England). *Analyst*, 1956, **81**, 417–426.—The sample is first separated from Th and brought into soln. in oxalic acid. To this soln. a niobium carrier and zirconium, strontium and cerium hold-back carriers are added and, after controlled acidification, the oxalate complexes are decomposed by boiling with $KClO_3$. The collected ppt. in oxalic acid soln. is treated with EDTA (disodium salt) to remove Zr, and Nb and Pa are pptd. with tannic acid. The ignited ppt. is dissolved in HNO_3 and HF, a soln. of Zr is added and barium zirconyl fluoride, carrying the Pa, is pptd. by addition of $Ba(NO_3)_2$. After purification by re-pptn., this ppt. is ignited and its gamma activity is measured in a scintillation counter. Alternatively, the Nb tannate ppt. is dissolved in HF and the Nb is separated from the Pa by upward diffusion paper chromatography, the solvent being a mixture of HF and ethyl methyl ketone. The dried strip is exposed to NH_3, dried, sprayed with tannic acid and dried again. The lower portion of the paper is then separated and its gamma activity is compared with that of a standard soln. of Pa on a similar strip.

A. O. Jones

472. **Chromatographic separation, detection and determination of selenium.** E. G. Weatherley (Rockware Glass Ltd., Rockware Ave., Greenford, Middx., England). *Analyst*, 1956, **81**, 404–408.—The chromatography of Se in association with 20

other elements has been investigated. Artificial mixtures, each containing 0·57% of SeO_2 mixed with various oxides, were used to represent silicate material, flue dust and electrolytic slime. After fusion of the sample with Na_2CO_3, an aliquot portion of the leached liquid was applied to a paper strip. The impregnated end of the dried strip was placed in the solvent mixture in an atmosphere satd. with the most volatile component of the solvent. Four solvent mixtures were found suitable, *viz*, acetone - HBr - ethanol, acetone - HCl - ethyl methyl ketone, ethyl methyl ketone - HBr and ethyl methyl ketone - HF. After upward diffusion of the solvent to 3·5 in. from the datum line, the air-dried strip was sprayed with a series of reagents. These are tabulated with the reactions obtained. For the determination of Se, standard chromatograms are made on a prepared sheet, the spraying reagent being thiourea, and the orange selenium band at the solvent front of the sample chromatogram is compared with these. The accuracy of the method is comparable with that of conventional methods at concn. between 0·1 and 1·0% of Se and is more rapid. A. O. JONES

473. **Spectrophotometric determination of selenium in stainless steels and in copper by 3:3′-diaminobenzidine [3:4:3′:4′-tetra-aminodiphenyl].** K. L. Cheng (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Chemist Analyst*, 1956, **45** (3), 67–68.—The method depends on the colour reaction of Se with a 0·5% soln. of 3:4:3′:4′-tetra-aminodiphenyl tetrahydrochloride. With stainless steel, the metal is digested with aqua regia, the soln. is adjusted to a pH of 2 to 3, and the reagent is added. With copper, the sample is dissolved in dilute HNO_3, the pH is adjusted to between 2 and 3, and the reagent is added. After 30 min. the pH is adjusted to between 6 and 7 with aq. NH_3 and the complex is extracted with toluene. The extinction of the extract is measured at 420 mμ. C. A. SLATER

474. **Chromatography on paper impregnated with ion-exchange resins. II. Separation of selenite and tellurite.** M. Lederer and S. Kertes (Inst. Radium, Paris, France). *Anal. Chim. Acta*, 1956, **15** (3), 226–230.—By using the procedure described in Part I (*cf. Anal. Abstr.*, 1955, **2**, 1445), conditions for the separation of SeO_3^{2-} from TeO_3^{2-} by partition chromatography on paper impregnated with Dowex-50 resin (colloidal form) have been established. The spots of 1% aq. Na_2SeO_3 and Na_2TeO_3 can be eluted with 0·005 to 0·5 *N* HCl, HBr, HNO_3, $HClO_4$ or H_2SO_4; after development of a 20-cm length the paper is sprayed with a soln. of $SnCl_2$ in 5 *N* HCl to reduce the two ions to the elements. The R_M value [= log $(1/R_F - 1)$] is related to the pH of the eluting acid by the equation $x\,\text{pH} = R_M + \text{const.}$ (x = ionic charge). The utility of this equation is discussed. W. J. BAKER

475. **Determination of chromium and vanadium in silica - alumina cracking catalyst.** T. A. Hiett and P. Kobetz (Shell Oil Co., Houston, Texas, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1495–1497.—In a modification of Parks and Agazzi's method (*Anal. Chem.*, 1950, **22**, 1179), samples are digested with HF and H_2SO_4 to remove Si, and with $HClO_4$ to oxidise Cr and V. The total content of Cr and V is determined by amperometric titration with Fe^{3+} solution, using a polarograph fitted with a S.C.E. reference electrode, salt bridge, constant-speed stirring motor, and rotating platinum indicator electrode. Then after reoxidation, chromium is selectively reduced with sodium azide, and the V is titrated directly. The Cr is calculated by difference. Results of assays are tabulated and compared with those of other modified procedures. The precision varies from within ± 0·0003% for <0·005% to ±1·0% of the mean for >0·10%. E. G. CUMMINS

476. **Diphenylcarbazone as an internal indicator in volumetric analysis. Determination of molybdenum by lead nitrate.** G. S. Deshmukh (Hindu Univ., Benares, India). *Bull. Chem. Soc., Japan*, 1956, **29** (1), 27–28 (in English).—A saturated soln. of diphenylcarbazone behaves as a reversible indicator in the titration of Pb with MoO_4^{2-}. *Procedure*—To the faintly acid soln. of Pb, 1 to 2 ml of indicator is added, followed by an equiv. amount of ethanol. On titrating the pink soln. with MoO_4^{2-}, the colour disappears, but re-appears at the end-point, when there is a rapid coagulation of $PbMoO_4$. The results are quant. and reproducible, so that it is possible to determine Mo quant. with $Pb(NO_3)_2$ as the primary standard. J. H. WATON

477. **The influence of certain substances present in the sample on the intensity of the molybdenum, indium and thallium lines.** L. A. Spektorov, I. K. Klavdienko and A. I. Pogulyaeva. *Izv. Akad. Nauk, SSSR, Ser. Fiz.*, 1955, **19** (1), 122–123; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,534.—The influence of compounds of K, Na, Li, Ba, Sr, Al, Zn, Cd, Hg, Cu and Fe on the intensity of the Mo, In and Tl lines in a mixture of MoS_2, $InCl_3$ or Tl_2SO_4 with carbon from a slot in the carbon electrode in an a.c. arc discharge is studied. The alkaline metals increase the intensity of the Mo lines, the other elements decrease it. The In and Tl lines are also strengthened by K, Na and Li, but are not altered in intensity by the other metals. C. D. KOPKIN

478. **Determination of trace elements in tungsten oxide by spectrographic cathode-layer and colorimetric methods.** N. Lounamaa. *Ann. Acad. Sci. Fenn., AII*, 1955, **63**, 1–93.—This dissertation includes the following sections. I. Introduction. II. Semi-quantitative spectrographic estimation of impurities in tungsten oxide. III. Quantitative spectrographic determination of some impurity elements in tungsten oxide. IV. Colorimetric and microvolumetric determination of some impurities in tungsten oxide. V. Practical application of the spectrographic method and its accuracy. N.E.

479. **Radioactivation analysis of arsenic in tungsten.** J. A. James and D. H. Richards (British Thomson-Houston Co. Ltd., Rugby, England). *Anal. Chim. Acta*, 1956, **15** (2), 118–121.—A radioactivation method has been devised for the determination of arsenic impurity in tungsten powder. Investigations to determine the minimum number of distillations required for radiochemical purity are described. W. C. JOHNSON

480. **Precipitation of uranium with arsanilic acid.** R. Pietsch (Inst. anorg. u. anal. Chem., Univ. Graz, Austria). *Z. anal. Chem.*, 1956, **152** (1–3), 168–171.—Although UO_2^{2+} are pptd. by excess of arsanilic acid (**I**), the ppt. contains varying amounts of H_2O; for the determination of U, the ppt. therefore has to be ignited to U_3O_8. No interference by Cl^-, NO_3^-, acetate or Na^+ is noted, but SO_4^{2-}, tartrate, oxalate and K^+ interfere. The method permits the determination of 18 to 250 mg of U to

within ± 0·5%; the separation of U from Pb (half its wt.); from Co, Cu, Ca, Sr and Ba (equal wt.); from Cd, Zn and Mg (fourfold excess); and from Ni (fivefold excess). *Procedure*—Add sufficient HNO_3 to the UO_2^{2+} soln. to prevent immediate pptn. on addition of **I**. Then add **I** (500 mg per 100 mg of UO_2^{2+}) in hot water, and dilute to 200 ml. Heat to boiling and add aq. NH_3 dropwise to pH 2·5. Boil for a few min. and filter. Wash the ppt. with hot water and ignite at 1000° (*cf.* Pietsch, *Ibid.*, 1955, **144**, 347). J. P. STERN

481. **Ion exchange of uranium.** T. Ishimori and H. Okuno (Dept. of Chem., Coll. of Sci., Rikkyo Univ., Tokyo, Japan). *Bull. Chem. Soc., Japan*, 1956, **29** (1), 78–82 (in English).—The adsorption of UO_2^{2+} is studied on cation exchangers in the presence of oxalic acid, Na acetate and Na_2SO_4, and on anion exchangers in the presence of HCl, $(NH_4)_2SO_4$, H_2SO_4 and Na_2CO_3. On a cation exchanger, the adsorption of UO_2^{2+} decreases rapidly with the increase of concn. of Na acetate, so that an acetate soln. may be used for eluting UO_2^{2+}. On an anion exchanger, the separation of U is possible in the presence of SO_4^{2-} and the strong tendency for UO_2^{2+} to adsorb in the presence of Na_2CO_3 may be used to concentrate U^{VI} that has been extracted with excess of Na_2CO_3. Separations of U from Th, Fe^{III} and Nd are described. J. H. WATON

482. **The determination of uranium by high-precision spectrophotometry.** A. Bacon and G. W. C. Milner (A.E.R.E., Harwell, Berks., England). *Analyst*, 1956, **81**, 456–469.—A procedure is described for the determination of the uranium content of relatively pure samples of U_3O_8 and uranium metal with a precision of ± 0·4%. The ignited sample is dissolved in HNO_3 and fumed with H_2SO_4, and the liquid is diluted to an appropriate vol. at a standard temp. (23°). Its extinction at 430 mμ is then determined against a reference soln. of accurately known uranium content. The effects of variations in chemical and spectrophotometric manipulations are discussed. A. O. JONES

483. **The spectrophotometric determination of uranium by means of the azide ion.** H. I. Feinsilber (U.S. Geol. Surv., Washington, D.C., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (3), 288–291.—Small amounts of U can be determined spectrophotometrically in dil. HNO_3 soln. by measuring the extinction of the yellow U - azide complex at 360 mμ. Beer's law is valid for concn. of U ≯ 2 mg per 25 ml; other metals, except those of the alkalis and alkaline earths, should be absent. *Procedure*—Evaporate the HNO_3 soln. of the sample (≡ ≃ 1 mg of U) to dryness and dissolve the residue in 5 ml of 7% v/v HNO_3. Make the soln. up to 25 ml with aq. 3 *M* sodium azide, and measure the extinction in a 1-cm silica cell (slit width 0·10 mm), with H_2O as reference. The concn. of U is calculated from the standard calibration curve. The procedure has a slightly higher sensitivity than the various thiocyanate methods and the colour is more stable. W. J. BAKER

484. **Analytical applications of the chemical action of light. III. New volumetric determination of uranium(VI) through photochemical reduction by lactic acid.** G. Gopala Rao, V. Panduranga Rao and M. V. Rama Rao (Andhra Univ., Waltair, India). *Anal. Chim. Acta*, 1956, **15** (2), 97–101.—Uranium acetate (0·0125 to 0·2 millimole) is mixed with lactic acid (≮ 4 mol. proportions), 5 ml of 5 *N* H_2SO_4 and sufficient water to produce 25 ml; the soln. is exposed in a Pyrex-glass beaker to a Philips Repro lamp and in 1 hr. the U^{VI} is reduced to U^{IV}. The U^{IV} is titrated with 0·25 *N* $NaVO_3$, the H_2SO_4 concn. being maintained at 6 *N*. N-Phenylanthranilic acid is used as indicator. The photochemical reduction is inhibited by Cl^- and Br^-; F^-, ClO_4^-, PO_4^{3-} and AsO_4^{3-} do not interfere. W. C. JOHNSON

485. **Potentiometric determination of fractional milligram quantities of uranium in zirconium.** L. Silverman and M. E. Shideler (Atomics International, Canoga Park, California, U.S.A.) *Anal. Chim. Acta*, 1956, **15** (2), 181–186.—A method is presented for the determination of U in quantities down to 0·1 mg and in the presence of Zr in amounts up to 1000 times that of the U. *Procedure*—Dissolve the metal sample in 5 ml of conc. $HClO_4$ with the aid of conc. HF and evaporate to a small vol. Add 5 ml of conc. HCl and dilute to 20 ml. Pass the soln. through a lead reductor (Sill and Peterson, *Brit. Abstr. C*, 1952, 541) into a mixture of 5 ml of conc. HCl and 2 ml of a 20% soln. of $FeNH_4(SO_4)_2.12H_2O$ in dil. H_2SO_4 (5%), wash the reductor with 20 ml of dil. HCl (10%) and titrate the contents of the receiver with standard sulphatoceric acid soln. W. C. JOHNSON

486. **Determination of uranium in iron.** L. Koste. *J. Stefan Inst.* (*Ljubljana*) *Rep.*, 1955, **2**, 7–8 (in English).—Very small concn. of U in iron and iron-base alloys are determined by an electrolytic method with a modified Mellaven cell in which the Fe, Cr and other constituents are eliminated on the mercury cathode with 4 amp. during a 2-hr. electrolysis. After electrolysis, $Al(NO_3)_3$ is added to the separated electrolyte and U is carried down as hydroxide by adding aq. NH_3. The ppt. is dissolved in HNO_3 and extracted with ethyl acetate. Fluorescent discs are prepared and the uranium content is determined with a transmission fluorimeter. CHEM. ABSTR.

487. **Effect of light petroleum on the separation of uranium in low-grade samples when cellulose columns are used.** D. Lebez and M. Ostanek. *J. Stefan Inst.* (*Ljubljana*) *Rep.*, 1955, **2**, 9–13 (in English).—The chromatographic method with cellulose columns for the separation of U is improved by the addition of light petroleum to the ether - HNO_3 solvent. The new solvent contains 20 ml of light petroleum, 190 ml of ether and 10 ml of HNO_3 (sp. gr. 1·42). For 25 to 30-cm high columns with 10 to 20 mm diam., 100 to 200 ml of solvent is used. Samples containing very small quantities of U give lower results with the chromatographic method than with the ethyl acetate extraction (*cf. Anal. Abstr.*, 1957, **4**, 486). The use of light petroleum enables 3 to 4 times more vol. of sample to be transferred without the aq. phase breaking through the column. Results as high as 90% of theoretical are obtained with siliceous ore samples. CHEM. ABSTR.

488. **Volumetric determination of fluorine in fluoroborates.** Z. T. Maksimȳcheva, Sh. T. Talipov and A. M. Koginova (V. I. Lenin Central Asia State Univ.). *Zavod. Lab.*, 1956, **22** (7), 791–794.—The soln. (100 ml) of BF_4^- containing the equivalent of ≯ 33 mg of HF is introduced into a flask, already containing 1 to 9 ml of 2% HCl soln. and fitted with a reflux condenser, and heated on a sand bath for 30 min. to 2 hr. according to the amount of HF and HCl. The condenser is then washed down with

a small amount of water, the soln. is neutralised with 2 *N* NaOH to Na alizarinsulphonate as indicator and then just acidified with 2% HCl soln., mixed with 1 ml of a buffer soln. (chloroacetic acid and NaOH), and finally titrated with 0·1 *N* $Th(NO_3)_4$. Hydrolysis in an alkaline medium gives low results, which gradually increase as the period of heating is continued. After 7 hr., results are still low by 8%. Acid hydrolysis as described shows insignificant errors. G. S. SMITH

489. **Organosilicon compounds. VII. Determination of chlorine or bromine attached to silicon.** Z. Šír and R. Komers (Dept. Org. Technol., Chem. Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 162–163.—For the determination of chlorine or bromine in organosilicon polymers, the sample is hydrolysed in a sealed tube with Na butoxide, and the resulting chloride or bromide can be determined by an argentimetric titration, with a visual, or preferably a potentiometric, indication of the end-point. A blank must be performed. J. ZÝKA

490. **Polarographic method for the qualitative and quantitative determination of chlorite ions.** E. Werner and N. Konopik (I Chem. Lab., Univ. Vienna). *Z. anal. Chem.*, 1956, **152** (1–3), 203–213.—On polarography (dropping-mercury electrode) in alkaline soln. (pH > 10), ClO_2^- give a characteristic double wave, the $E_{\frac{1}{2}}$ of which becomes more negative with increasing pH. The height of the wave increases very suddenly at pH 14. This permits identification of ClO_2^- (5×10^{-5} *M*) in the presence of Cl^-, ClO_4^-, ClO_3^- and ClO^- (*M*). The polarographic curve in alkaline media is unsuitable, but in almost neutral soln. with $CaCl_2$ or $LaCl_3$ as electrolytes, polarography is highly suitable for the determination of ClO_2^-. The method is most valuable because of its high specificity (*cf.* Konopik and Werner, *Monatsh.*, 1955, **86**, 937). J. P. STERN

491. **Titanometric estimation of chlorate.** R. Weiner (Chlorat-Chemie, G.m.b.H., Innsbruck, Austria). *Z. anal. Chem.*, 1956, **153** (1), 27–29.—Chlorates can be determined quant. by titration with $TiCl_3$ if care is taken to prevent losses in the form of gaseous ClO_2. *Procedure*—After expelling the air from the flask with CO_2, excess of $TiCl_3$ soln. is added rapidly to the chlorate soln. The flask is corked and allowed to stand, with occasional shaking, for 3 min. Once again CO_2 is passed through the flask, and the excess of $TiCl_3$ is back-titrated with ferric ammonium sulphate soln., with thiocyanate as indicator. J. H. WATON

492. **Determination of microgram quantities of free iodine using o-tolidine reagent.** J. K. Johannesson (City Council Lab., Wellington, New Zealand). *Anal. Chem.*, 1956, **28** (9), 1475–1476.—To 25 ml of aq. test soln. containing free iodine (< 3 p.p.m.) and iodide (< 50 p.p.m.) is added 1 drop of a saturated soln. of $HgCl_2$, followed by 0·5 ml of acid *o*-tolidine soln. The extinction is measured at 425 mμ within 10 min. The procedure is subject to interference from other oxidising agents, with the exception of iodate. With 4·0-cm absorption cells, 0·1 p.p.m. of iodine may be determined with a sensitivity within ± 5%. E. G. CUMMINS

493. **Absolute alpha counting of astatine-211.** J. K. Basson (Brookhaven Nat. Lab., Upton, L.I., N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1472–1474.—The absolute standardisation of the α-emitter astatine (^{211}At) has been achieved by dissolving the isotope in the liquid scintillator of a scintillation counter. Up to 25% of H_2O can be tolerated in the chosen scintillator, *p*-dioxan containing 2:5-diphenyloxazole (50 g per litre). E. G. CUMMINS

494. **Argentic oxide as an oxidimetric reagent. Determination of manganese, cerium and chromium.** J. J. Lingane and D. G. Davis (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (3), 201–206.—A rapid determination of Mn and Cr in ferrous and non-ferrous alloys and of Ce in "misch metal" can be made by adding a small excess of AgO to a cold aq. soln. of Mn^{2+}, Ce^{3+} or Cr^{3+} in 2 to 5 *M* HNO_3 or $HClO_4$, diluting and warming (≃ 80°) the soln. to reduce the excess of Ag^{2+}, and then titrating the MnO_4^-, Ce^{4+} or $Cr_2O_7^{2-}$ with a standard soln. of Fe^{2+}. If the titration is made potentiometrically, the destruction of Ag^{2+} by heating is unnecessary, since the second inflection on the curve represents the true end-point. The accuracy is within ± 0·2%; Tl and Co interfere. W. J. BAKER

495. **The ferric complex salt of formyldeoxybenzoin.** Seishi Takagi and Hiroyuki Yasuda (Pharm. Inst., Medical Faculty, Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (6), 655–656.—The purple-brown ppt. produced by the reaction between Fe^{3+} and formyldeoxybenzoin (**I**) in an ethanolic soln. is specific for Fe^{3+} (limit of detection, 1 μg of Fe in 0·05 ml). Precise experimental conditions were examined and it was found that the complex having the formula FeI_3 is formed quant. in a soln. of pH 3·8 to 7·0 in the absence of complex-forming anions such as PO_4^{3-} or F^-. No interference results from the presence of other metal ions, including those of Cu, Ni and Co. K. SAITO

496. **Oxidimetric determination of ferrous iron in the presence of bromide.** H. Schäfer and R. Gruehn (Univ. Münster, Westphalia, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 172–177.—In the oxidimetric determination of Fe^{II}, formation of free Br must be avoided to prevent the 'induced' oxidation of Fe^{II}. In titrations with $KMnO_4$, interference by ≯ 100 mg of Br^- is suppressed by addition of Mn^{2+}, but 500 mg of Br^- still interferes. In titrations with $K_2Cr_2O_7$, high dilutions reduce interference by Br^-. Thus with Na N-methyldiphenylaminesulphonate (**I**) in H_3PO_4 as indicator, a 0·005 *N* soln. of Fe^{II} containing 500 mg of Br^- may be determined with an accuracy within ± 0·2%. In titrations with $Ce(CO_4)_2$ there is no interference due to Br^- with ferroin or **I** as indicator. J. P. STERN

497. **Volumetric titration of iron(III) salts with disodium EDTA, using iron(II) - cacotheline as indicator.** G. Gopala Rao, V. Narayana Rao and G. Somidevamma (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **152** (5), 346–350 (in English).—Titration of Fe^{III} with EDTA (disodium salt) at pH 4 to 5 in a CO_2 atmosphere and with Fe^{II} - cacotheline indicator to a pink end-point (due to the reduction of cacotheline by Fe^{II} - EDTA) permits the determination of 10^{-5} to $1{\cdot}6 \times 10^{-4}$ mole of Fe^{III} with an accuracy within ± 1%. Ferrous ions do not interfere, but Na_2HPO_4 interferes. J. P. STERN

498. **The volumetric determination of ferric ions with triphosphoric acid.** L. Jankovits (Technol. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62**

(6), 191–195.—Dilute the weakly acidic Fe^{3+} soln. (corresponding to 5 to 50 ml of titrating soln.) to $\simeq$ 90 ml with H_2O. Add citrate buffer (pH 2·5) (1 ml) and Variamine blue ($\simeq$ 0·3 g) and titrate slowly with 0·01 or 0·02 *M* $Na_5P_3O_{10}$ (**I**) soln. until the violet - red soln. becomes colourless. The prep. of **I** is described; its soln. is stable for 15 to 20 days. Each mol. of **I** complexes with one Fe^{3+}. All ions that form a complex with **I** interfere. The experimental error is always negative.

A. G. PETO

499. **Ultra-violet spectrophotometric determination of iron.** M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa (Chem. Dept., Fac. of Sci., Univ., Kyoto, Japan). *Bull. Chem. Soc., Japan*, 1956, **29** (1), 57–60 (in English).—The presence of isosbestic points at 223 and 271 mμ for $Fe(ClO_4)_3$ soln. is confirmed. A spectrophotometric method for determining Fe in the concn. range 0 to 20 p.p.m. is studied, in which the extinction of the perchlorate soln. is measured at 271 mμ. Because of the somewhat low sensitivity of the method, the procedure is better adapted to the differential estimation of Fe in the concn. range 50 to 70 p.p.m. at a pH of $\simeq$ 2·5 to 3·5 at 270 mμ against a blank soln. containing 50 p.p.m. of Fe. The method can be carried out in the presence of Na, Ni, Co, Zn, Mn and Al, but Cu and Ti^{IV} cause interference if present in amounts $>$ 10 p.p.m. The presence of Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} also causes interference. The method is successfully applied to the determination of Fe in iron-base alloys. *Procedure*—The sample (150 to 200 mg) is dissolved by warming with 4 *N* $HClO_4$. After cooling, drops of H_2O_2 (30%) are added, and the soln. is evaporated almost to dryness several times. The residue is dissolved in water and is diluted to 500 ml. A 20-ml aliquot is diluted to 100 ml and the extinction is measured at 270 mμ with a soln. of Fe (50 p.p.m.) as blank. The errors in the estimation are 0·2 to 0·3%.

J. H. WATON

500. **2:4-Dihydroxybenzoic acid as a reagent for spectrophotometric determination of ferric iron.** S. Vivarelli (Anal. Chem. Inst., Florence Univ., Italy). *Chim. e Ind.*, 1956, **38** (6), 461–465.—Between pH 2·7 and 3·3 the ferric - 2:4-dihydroxybenzoic acid complex has max. extinction at 510 mμ and is suitable for the determination of 1·0 to 45 p.p.m. of iron. Ions that interfere with the complex are studied; a comparison is made with 16 different reagents for Fe^{II} and Fe^{III}. Extinction curves are given.

C. A. FINCH

501. **Photometric determination of iron in pure metals, alloys and ores after separation by partition between two solvents.** H. Specker and W. Doll (Inst. Spektrochem., Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 178–185.—*iso*Butyl methyl ketone (**I**) quant. extracts Fe^{III} from 5·5 to 7 *N* HCl (partition coeff. $>$ 1000) and offers advantages over ether as solvent. This permits separation of Fe^{III} from Cu, Zn, Ni, Al, Mg, etc., and facilitates the determination of traces of Fe in metals. Re-extraction with water quant. recovers the Fe, which is then determined by photometry as the *o*-phenanthroline complex. The method is used for the determination of Fe (0·1%) in Al, Mg, Ni and brass, and of Fe (0·001 to 0·02%) in Cu, Zn, brass and pure Ni (with Fe added). The accuracy is within ± 2%. Tin interferes. *Procedure*—Dissolve the sample (0·1 mg of Fe) in HCl and some drops of HNO_3, evaporate to dryness, remove Si with HF, and dissolve the residue in 5·5 *N* HCl (total 25 ml). Extract with 25 ml of **I**, separate, reject the aq. phase, and wash the org. phase with 5·5 *N* HCl. Then extract with 25 ml of water and determine the Fe in the aq. phase.

J. P. STERN

502. **Studies in chemical analysis and separation by extraction methods. IV. Extraction of iron and molybdenum from their mixed solution.** Sakujiro Yamamoto (Faculty of Liberal Arts, Shimane Univ., Matsue). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 713–716.—Extraction of Fe and Mo chlorides from their HCl soln. was studied with butyl acetate. The lower the temp., the better the efficiency of extraction. By repeating the extraction at 10°, 99·9% of Fe and 99·5% of Mo can be extracted from 7·5 *N* HCl. Their fractional extraction from an acid soln. met with little success, even in the presence of a masking agent for either of them.

K. SAITO

503. **Determination of iron in titanium sponge, alloys, and ores. Automatic derivative spectrophotometric titration with electrolytically generated titanous ion.** H. V. Malmstadt and C. B. Roberts (Univ. of Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1412–1416.—After dissolution in hot dilute H_2SO_4 or H_2SO_4 - HBF_4 soln., the sample is treated with MnO_4^- to oxidise Fe^{2+}, the excess of MnO_4^- being destroyed with N_2^-. To the soln. is added leuco methylene blue and the soln. is transferred to an automatic derivative spectrophotometric titration apparatus (*cf. Anal. Abstr.*, 1957, **4**, 763), into the cell of which are inserted the electrodes of a device for the quantitative generation of Ti^{3+} from the Ti^{4+} of the soln. (full details are provided for its construction). The titration is run fully automatically at 665 mμ, and the iron content is deduced from the quantity of electricity employed. An absolute precision of ± 0·003% is claimed, and the time of determination is much reduced.

D. A. PANTONY

504. **Increase of precision in spectrochemical analyses of steels obtained by the use of electronically controlled high-voltage spark sources.** Á. Bardócz and F. Varsányi. *Acta Tech. Acad. Sci., Hung.*, 1955, **13** (3–4), 409–420 (in English).—Two electronically controlled high-voltage spark sources and a rotary synchronous interrupter-controlled switch source are compared under identical conditions for steel analyses. The electronically controlled source of 100-cycles sparking frequency yields higher reproducibility and more uniform results for the individual elements, while the source of 50-cycle sparking frequency yields the same reproducibility as the rotary switch controlled source. The mean deviation resulting from two tests of 20 measurements each is ± 1·7 and ± 1·8%, respectively, referred to the alloy content present for the 100-cycle sparking frequency, as compared to ± 2·9% obtained with the other two sources, by using in each case a Hilger, large Littrow-type spectrograph with quartz optics, a 30-μ slit width, a 1-mm slit height, a 21,000-V peak source, 10,000-picofarad capacitance, flat-surfaced samples with spectroscopically pure carbon counter-electrodes, a 3-mm spark gap, 1-min. presparking, and 2- or 4-min. exposures. Straight-line working curves were obtained for the line pairs Si 2881·6 - Fe 2929·0, Mn 2933·1 - Fe 2689·2, Ni 3414·8 - Fe 3417·8, Mo 2816·2 - Fe 2828·6, and V 3093·1 - Fe 3009·6.

CHEM. ABSTR.

505. **Determination of the carbon content of steel from the hardness of quenched samples.** M. G. Pyatigorskiĭ (Stalingrad Agric. Inst. and the "Red October" Works). *Zavod. Lab.*, 1956, **22** (7), 778–781.—The method enables the carbon content of carbon and alloy constructional steel during the time of the melt to be determined in 1·5 to 2 min. with an accuracy of the same order as that of the rapid combustion method. The sample of liquid steel is poured into a special mould which produces a rod of square section. The mould is so designed that when the rod is removed it has cooled to only $\simeq 1100°$. The sample is then plunged into ice and water ($\not> +5°$) for 3 to 5 sec. Two opposite parallel surfaces are then cleaned with emery paper on a horizontal disc of 150 to 200 mm diameter revolving 700 to 1000 times a min. The surfaces are dipped in water and the Rockwell hardness is measured at three or four points along the length of each surface. From the max. value of the hardness the carbon content is obtained from data of samples of known content. The curve relating hardness and content is similar for carbon, nickel and chromium steels, is nearly linear from 0·11 to 0·4%, and is applicable up to 0·52% of carbon.

G. S. Smith

506. **Gasometric determination of carbon in ferrous alloys.** E. Dubox. *Ind. y Quim.*, 1955, **17**, 411–418, 425.—A review is given of methods of determining C in steel and ferrous alloys, and the gasometric method (burning in O, removing the SO_2 formed, and measuring the volume of CO_2 produced) is described with details of the principles, apparatus, technique and calculations.

D. Leighton

507. **The photocolorimetric determination of silicon in steel.** [**Symposium on problems of the oil industry.**] V. K. Chudinov. *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,408.—To the sample of steel (0·2 g) add HNO_3 (sp.gr. 1·10) (10 ml), cover the beaker and heat to boiling point on a hot-plate; then remove the beaker to the edge of the hot-plate and continue boiling for 3 to 5 min. (the vol. after boiling must be $\not< 8$ ml). Transfer the soln. to a 30-ml flask and dilute to the mark with water. Transfer 1 ml of the soln. to a flask of similar capacity, add 5% ammonium molybdate soln. (3 ml), mix, and allow to stand for 3 to 4 min. for the formation of the yellow molybdosilicate complex. Then add H_2SO_4 (1:3) (5 ml), mix, make up to the mark with a 6% soln. of $(NH_4)_2SO_4.FeSO_4.6H_2O$, set aside for 5 min. and measure the extinction in a 20-mm cell, with a red filter. A blank is carried out with all the reagents, and calibration curves are constructed.

C. D. Kopkin

508. **Determination of tin in steel, pig iron, alloy steel and iron ore.** Takuho Ikegami, Kazuo Suematsu and Ohiko Kammori (Tech. Res. Inst., Yawata Iron and Steel Works, Yawata). *Japan Analyst*, 1956, **5** (7), 379–383.—Tin (0·002 to 0·1%) in steel, ferro-alloys and iron ores is co-pptd. with MnO_2, dissolved in HCl containing H_2O_2, reduced with a mixture of $HgCl_2$ and NaH_2PO_2 and titrated with iodine soln. The presence of W, Ti, Mo (each $< 0{\cdot}5\%$), Cu ($< 0{\cdot}6\%$) and Cr does not cause interference. When V (> 5 mg) is present, the MnO_2 is re-pptd. Elementary As (> 5 mg) precipitates on the reduction with NaH_2PO_2; the soln. is filtered and then similarly titrated. The time taken for an estimation is < 40 min. *Procedure*—The sample (2·5 g; for $< 0{\cdot}01\%$ of Sn, 5 g) is dissolved in HNO_3 (1 + 1, 40 ml) and treated with $MnSO_4$ (5%, 10 ml) and $KMnO_4$ (3%, 5 ml) while boiling until all the $KMnO_4$ is decomposed. The MnO_2 is filtered off, washed with hot water, dissolved in warm HCl (1 + 1, 20 ml) containing a few drops of 3% H_2O_2 and boiled with conc. HCl (50 ml) and H_2SO_4 (1 + 1, 50 ml) to decompose the excess of H_2O_2. Saturated $HgCl_2$ soln. (1 ml) and NaH_2PO_2 (5 g) are added to the strongly acid soln., which is refluxed for 5 min. in a current of CO_2. The product is cooled and titrated with $N/60$ iodine soln., with 1% starch soln. (5 ml) as indicator. High-chromium steel is dissolved in dil. H_2SO_4 (1 + 6) and treated with HNO_3 and $KMnO_4$, then with $MnSO_4$ to ppt. MnO_2. Iron ore (1 g) is fused with Na_2O_2 (5 g), leached with water, neutralised with HNO_3 (1 + 1) and made acid with HNO_3 (1 + 1, 20 ml, containing 3% H_2O_2). This soln. is treated with $MnSO_4$ and $KMnO_4$ as described above. High-speed steel of high tungsten content is dissolved in H_2SO_4 (1 + 1, 10 ml) and HCl (1 + 1, 50 ml) and treated with HNO_3 (1 + 1, 20 ml); the ppt. of WO_3 is filtered off and the filtrate is heated to white fumes before being treated as above.

K. Saito

509. **Colorimetric determination of nitrogen in steels.** E. J. Dubox and A. H. Mayoral (Laboratory and Process Dept., Siam di Tella Ltda., Argentina). *An. Asoc. Quim. Argent.*, 1955, **43** (4), 227–237.—Factors influencing the colorimetric analysis of N in steels are examined—the acid for dissolving the sample, amount of alkali needed, apparatus and method of attack, volume of distillate, size of sample, final concn. of acid, and sensitivity of the process. The technique evolved is discussed and described. To a 0·5-g sample in a 500-ml distilling flask is added 30 ml of dil. H_2SO_4 (1:2) and the whole is heated until acid fumes are liberated. The flask is cooled and 40 ml of water is added. The flask is connected to a condenser and also closed by a plug through which passes a thistle funnel, the end dipping below the liquid surface. Through the funnel is added 50 ml of 30% NaOH, slowly and with shaking, and the liquid is heated. The distillate (35 ml) is nesslerised. The deviation is less than 0·002% of N and the precision is 0·025 mg.

D. Leighton

510. **Photometric determination of vanadium in steel and ferro-alloys by a diphenylaminesulphonate method.** Tsutomu Fukazawa and Shizo Hirano (Inst. of Techno-anal. Chem., Faculty of Eng., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1956, **5** (6), 336–340.—The colorimetric determination of V with Na diphenylamine-sulphonate (**I**) was applied to the analysis of steel and ferro-alloys. For a stable colour, the concn. of H_2SO_4 (20 ml), H_3PO_4 (15 ml) and Fe (0·05 to 0·4 g) in the final soln. (100 ml) should be carefully adjusted. The presence of a large amount of Cu (> 100 mg), Ni (> 120 mg), Co (> 40 mg) and Cr (> 3 mg) in the final soln. causes fluctuation of results. For the analysis of carbon steel, most Fe should be removed by mercury-cathode electrolysis. *Procedure*—The sample (0·1 g) is attacked with a mixture (1 + 1 + 1, 15 ml) of H_2SO_4 (1 + 1), HNO_3 (1 + 1) and H_3PO_4 [when necessary, 0·3 to 0·5 g of $(NH_4)HF_2$ is added] until white fumes are evolved. The product is mixed with H_2SO_4 (1 + 1, 35 ml), H_3PO_4 (10 ml) and urea soln. (20%, 5 ml). A few drops of 0·1 *N* $FeSO_4$ are added to reduce higher oxides, and V in the soln. is oxidised with 1·5% $KMnO_4$. The excess of $KMnO_4$ is decomposed by adding 3% $NaNO_2$, dropwise; 0·05% **I** soln.

(2·0 ml) is added and the whole is made up to 100 ml. The extinction is measured at 562 mμ and again after the addition of $FeSO_4$ (0·1 *N*, 2 to 3 drops) to the photometric cell, the amount of V being calculated from the difference in the two measurements. Ferro-silicon, -titanium and -tungsten are decomposed with HF (40%) and treated as described above. For the analysis of ferromanganese, V is co-pptd. with $Fe(OH)_3$ with aq. NH_3 soln., the ppt. is dissolved in HCl (1 + 2), re-pptd. and dissolved in H_2SO_4 before being treated as above. The Cr in ferrochromium is removed as chromyl chloride by treatment with $HClO_4$ and NaCl. K. SAITO

511. **Determination of phosphorus in ferrous metals without taking drillings.** N. A. Tananaev and I. A. Korobova (S. M. Kirov Ural Polytech. Inst.). *Zavod. Lab.*, 1956, **22** (8), 916–917.—A portion of the surface of a sample of low-alloy steel or cast iron confined by a paraffin-wax ring is treated with a few drops of HNO_3 in parallel with a standard. After cessation of reaction the surfaces are washed with water and dried with filter-paper. The cleaned surfaces are each treated with 10 drops of HNO_3 and after the reaction has ceased the solutions are transferred to test-tubes by means of a pipette. The surfaces are washed several times with a few drops of water and the washings are added to the main soln. The solutions are mixed with 10 drops of dil. HNO_3 (1 + 1), boiled for 1 to 2 min., then treated with 3 to 4 drops of 1% $KMnO_4$ soln. and again boiled. The pptd. MnO_2 and excess of $KMnO_4$ are reduced by the addition of 1 to 2 drops of 10% $NaNO_2$ soln., the soln. are again boiled, then cooled and transferred to 10-ml graduated cylinders. Water (3 to 4 ml) and 1 ml of a molybdate - vanadate mixture are added, and the colour intensity is measured. The use of the mixed reagent, which is stable for one month, is preferred to that of addition of the reagents separately, since there is less interference from silicates. For P over the range 0·017 to 0·084% the max. errors found were +0·004 and −0·003, and with cast irons of content 0·42 to 0·50% the max. errors were +0·010 and −0·013.
G. S. SMITH

512. **Determination of oxygen in cast iron.** H. Gotô, S. Susuki, J. Kimura and A. Onuma. *Tetsu to Hagane*, 1956, **42** (1), 49–52.—Successful results, in comparison with standard specific methods for each inclusion, were obtained in determining each oxide in cast iron by a fractional vacuum-fusion method. A tin bath was used; FeO, MnO, SiO_2 and Al_2O_3 were extracted at 1050°, 1150°, 1450° and 1750°, respectively. J. IRON ST. INST. ABSTR.

513. **Detection of cobalt with alkali thiocyanate and tri-*n*-butylamine.** M. Ziegler and O. Glemser (Anorg.-Chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **152** (4), 241–245.—Reaction of alkali tetrathiocyanatocobaltiate, $K_2[Co(SCN)_4]$, with tri-*n*-butylamine gives the deep-blue tri-*n*-butylammonium tetrathiocyanatocobaltiate (**I**); this forms the basis of the method for the detection of small amounts of Co. The salt **I** is insol. in water but readily sol. in org. solvents. The method is very sensitive; 0·5 μg of Co is detectable at a limiting concn. of 1 in 3×10^6. Elements that interfere are masked, thus Fe, V, U and Bi are masked with NaF and $Na_2S_2O_3$, and Cu^{II} is reduced to Cu^{I}, which does not interfere. Nickel gives a green colour and in 100-fold excess interferes, but 1 μg of Co can be detected in the presence of 50 mg of Fe. *Procedure*—Add to the neutral or weakly acid sample some conc. aq. $Na_2S_2O_3$ soln., then a few drops of 50% aq. KSCN and some solid NaF. Add tri-*n*-butylamine (1 to 2 drops), shake, and add *N* H_2SO_4 (1 to 2 drops). A blue colour in the tributylamine phase indicates the presence of Co. The colour is more readily visible on addition of amyl alcohol. Tri-*n*-butylammonium acetate soln. of pH 3 to 4 may be used instead of the free base and addition of H_2SO_4 is not then necessary. J. P. STERN

514. **Detection of cobalt with alkali cyanate and tri-*n*-butylamine.** M. Ziegler and O. Glemser (Anorg.-Chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **152** (4), 245–248.—Salts such as KSCN, KCNO, KSeCN and KN_3, in general, give coloured complexes with tri-*n*-butylamine and Co^{2+}, Cu^{2+}, Fe^{3+}, Pd^{2+}, UO_2^{2+}, Cr^{3+}, Rh^{3+}, Ru^{3+} and Os^{3+}. Tri-*n*-butylammonium cyanatocobaltiate, a blue water-insol. complex, is useful for the detection of Co (1 μg) at a limiting concn. of 1 in 10^6 and in the presence of excess of Fe^{III} (1000 parts) and of Ni (8000 parts). For very large amounts of Fe^{III} (10^5 parts), NaF is used as masking agent and this also obviates interference by Bi (35,000 parts), Mo (5000 parts), W (1000 parts) and UO_2^{2+} (5000 parts). *Procedure*—To the weakly acid sample add $(NH_4)_2SO_4$ (40 to 50 mg), 25% KCNO soln. (3 drops) and tri-*n*-butylamine (1 to 2 drops) and shake. Then shake with amyl alcohol (2 to 3 drops) while adding HCl to a pH of 1 to 2 A blue colour in the non-aqueous phase indicates Co.
J. P. STERN

515. **The nitroso-R salt method for the determination of cobalt in ores.** B. D. Guerin (Metallurgy Dept., Univ. Melbourne, Australia). *Analyst*, 1956, **81**, 409–416.—The colorimetric nitroso-R salt method for the determination of cobalt has been critically examined. By the procedure developed, Co can be rapidly and accurately determined in ores without chemical separations. The ore is dissolved in HNO_3, fumed with H_3PO_4 and H_2SO_4 and the cooled digest is dissolved in water. The soln. is treated with sodium acetate and a 1% soln. of nitroso-R salt and boiled for 1 min., and again after addition of dil. HNO_3. After suitable dilution, the extinction of the filtered soln. is measured in a Spekker absorptiometer and compared with that of a standard by the differential method described by Milner *et al.* (*Anal. Abstr.*, 1954, **1**, 2645). Iron in large amounts causes slightly high results and when the ore is suspected to contain more than 30%, smaller sample wt. should be used. No other knowledge of the composition of the ore is necessary
A. O. JONES

516. **Measurement of the amount of cobalt co-precipitated with hydrated ferric oxide. I. The amount of cobalt co-precipitated from hydrochloric acid solution.** Michio Mashima (Faculty of Eng., Niigata Univ., Nagaoka, Niigata Prefecture). *Japan Analyst*, 1956, **5** (6), 319–322.—Co-pptn. of Co with $Fe(OH)_3$, obtained by the treatment of their dil. HCl soln. with ZnO, was studied by means of radioactive ^{60}Co. The amount of co-pptd. Co increases with increase in the total amount of Co; the loss is $\simeq 3\%$ for 0·5% of Co in Fe and $< 1\%$ for $> 3\%$ of Co, being markedly less than with aq. NH_3 soln. as precipitant.

II. The effect of cupric chloride and sulphuric acid. Michio Mashima. *Ibid.*, 1956, **5** (6), 322–324.—Similar experiments were carried out for pptn. from an HCl soln. containing Cu and from dil. H_2SO_4 soln. The amount of co-pptd. Co

increases 2 to 3 times with increasing content of Cu, but remains const. for amounts of Cu $> 2\%$. A similar trend is observed for pptn. of $Fe(OH)_3$ from an H_2SO_4 soln. K. SAITO

517. **Chromatographic determination of cobalt in zinc plating solutions.** E. Bertorelle and E. Paglia (Chem. Metall. Centre, Ind. Chem. Inst., Milan Univ.). *Chim. e Ind.*, 1956, **38** (5), 384–385.—In the method proposed, Mn present is previously eliminated by co-precipitation with sodium dithionite in ammoniacal solution in the presence of ammonium chloride. Ascending paper chromatography is then employed, and the results are compared with a standard scale. The solvent used is acetone - ethyl methyl ketone - water - conc. HCl (85:5:5:5), and the paper is developed with a mixture of nitroso-R salt (0·5 g), glycerol (100 ml), HCl (1 ml) and ethanol (100 ml). Full details of procedure, and a standard scale, are given.
C. A. FINCH

518. **The solubility of dimethylglyoxime and its nickel complex in alcohol - water mixtures.** A. K. Babko and P. B. Mikhel'son. *Ukrain. Khim. Zhur.*, 1955, **21**, 588–593; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,352.—It is experimentally established that with ethanol (**I**) concn. of 0, 9·6, 19·2, 28·8, 38·4, 48·0, 57·6, 67·2, 76·8, 86·4 and 96% by vol., in ethanol - water mixtures, the solubility of dimethylglyoxime (**II**) is, respectively, 4·4, 5·6, 7·1, 11, 17, 26, 44, 70, 92, 111 and 121 millimoles per litre. It is found that the solubility of the nickel - dimethylglyoxime complex (**III**) in the presence of **I** is increased at first more markedly and then more weakly, and at a concn. of **I** $\lessapprox 48\%$ is equal to $1{\cdot}5$ to $2{\cdot}1 \times 10^{-2}$ mole per litre. In the presence of excess of **II** the solubility of **III** is lowered; on introducing **II** to saturation of suitable water - ethanol mixtures the solubility of **III** is $< 2 \times 10^{-7}$ mole per litre. The solubility of **II** in ten organic solvents is studied. The solubility of **II** in CCl_4, $CHCl_3$, *iso*butyl alcohol and ether is, respectively, 6×10^{-5}, 4×10^{-4}, $3{\cdot}8 \times 10^{-3}$ and $9{\cdot}9 \times 10^{-2}$ mole per litre. The dispersion coeff. between water and an organic solvent for **II** is somewhat different from the ratio of the solubilities of **II** in these solvents; however, the mol. constitution of **II** is the same in water and organic solvent. The solubility series for **III** is often the reverse of that for **II**.
C. D. KOPKIN

519. **Ultra-violet spectrophotometric determination of nickel with benzil α-dioxime.** Yasumitsu Uzumasa and Shigenari Washizuka (Dept. of Chemistry, Fac. Sci., Hokkaido Univ., Sappora). *Bull. Chem. Soc. Japan*, 1956, **29** (3), 403–407 (in English).—By extracting Ni as the benzil α-dioxime complex with $CHCl_3$, treating with alkali and measuring the extinction at 275 mμ (maxima at 358 and 406 mμ are less sensitive), a precise method for estimating microgram quantities, virtually free from interference by elements other than Co, is claimed. To about 15 ml of slightly acid solution containing up to 20 μg of Ni, buffered with a few ml of Na tartrate or citrate (10%) and made just alkaline with aq. NH_3, add 2 ml of 0·02% benzil α-dioxime solution. Shake for 10 sec., add 5 ml of $CHCl_3$ and shake for 2 min. Extract the ppt., draw off the aqueous layer and to the $CHCl_3$ solution add 1% NaOH solution (10 ml). Shake for 1 min., draw off the aqueous layer, repeat with 0·5% aq. NH_3 (10 ml) and then with 1% NaOH solution (2×10 ml). Filter the $CHCl_3$ solution through a dry paper into the spectrophotometer cell and determine Ni with the aid of standard solutions of Ni and a blank (water) treated in an identical manner. With 5 μg of Ni, up to 10 μg of Co or 100 μg of Cu can be tolerated; the influence of Cu above this level can be avoided by increasing additions of the reagent and $CHCl_3$. J. O. LAY

520. **Studies on the platinum group. VI. The reaction of rhodium with 1-nitroso-2-naphthol and its use for the determination of rhodium.** Kiyoshi Watanabe (Oizumi Seisakusho, Nerima-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (4), 547–550.—Rhodium reacts with 1-nitroso-2-naphthol (**I**) in a weakly acid soln. to give a red - brown ppt. (limit of detection 0·5 μg). The pptn. is quant. at pH 4·8 to 5·6 at $> 70°$, the composition of the ppt. being RhI_3 in the presence of **I** in an amount > 8 times that equiv. to the Rh. The ppt. is converted into Rh_2O_3 by ignition at 800°. An acid sample soln. is diluted to $\simeq 100$ ml and treated with **I** soln. (1% in 50% acetic acid, $\simeq 150$ ml) and made pH 4·8 with aq. NH_3 soln. The product is boiled for 15 min. and cooled, the ppt. being washed with 20% acetic acid and water and ignited. When the pH value increases to > 6 during the digestion of the ppt., other metals of the platinum group are pptd., but Pd gives a similar ppt. under the given conditions.

VII. Colorimetric method. Kiyoshi Watanabe. *Ibid.*, 1956, **77** (7), 1008–1011.—The ppt. obtained as above is sol. in organic solvents, including acetone and benzene. The absorption curve varies with the solvent, but is almost identical in acetone and benzene (max. 420 mμ). The extinction obeys Beer's law for 0·9 to 18 μg of the complex, per ml of solvent. Interference results from Pd, Ru, Fe, Co and a large amount of Pt. The ppt. obtained as described above is filtered off, washed, dried and dissolved in acetone for measurement of the extinction.
K. SAITO

521. **The detection of palladium with violuric acid.** M. Ziegler and O. Glemser (Univ. Göttingen, Germany). *Mikrochim. Acta*, 1956, (7–8), 1152–1154.—By the addition of a 0·2% aq. soln. of violuric acid to a weak HCl soln. of Pd^{II} a yellow - brown ppt. or turbidity is formed within 5 min. The limit of detection is 1·5 μg of Pd and of concn. 1 in 300,000. The reaction is specific for 2 μg of Pd in the presence of Pt^{4+} (× 130), Rh^{3+} (× 70), Au^{3+} (× 250) and Pb^{2+} (× 2000). Investigation of the palladium compound showed that the metal is bound with two radicals of violuric acid.
D. F. PHILLIPS

522. **A direct microheterometric determination of palladium with 1-nitroso-2-naphthol in excess of foreign metals. A study of the reaction and the working conditions.** M. Bobtelsky and B. Mayer (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **15** (2), 164–172.—Solutions containing 0·2 to 0·5 mg of Pd as chloride or nitrate in 20 ml of water and 10 ml of ethanol, acidified with 1 ml of *M* HNO_3, are titrated heterometrically (*Anal. Abstr.*, 1954, **1**, 1770) with a 0·005 *M* soln. of 1-nitroso-2-naphthol in ethanol. The end-point is obtained when 3 mol. equiv. of the reagent have been added. The presence of Cl^- in high concn. must be avoided. The ions of most common metals may be present in large excess, but the amount of Co^{2+} present should be restricted and Cu^{2+} must be absent. If Fe^{3+} are present, tartaric acid is added.
W. C. JOHNSON

523. **Analytical chemistry of platinum metals. II. Microchemical detection of osmium with phosphonium and arsonium compounds.** R. Neeb (Univ. Mainz, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 158–162.—Osmium, like most other platinum metals, in HCl soln. gives insol. cryst. ppt. with certain arsonium and phosphonium compounds. Since distillation separates Os and Ru from the other platinum metals and Ru in HCl does not give a ppt. with these reagents, this method is valuable for the rapid detection of Os. In HBr soln. Ru occasionally gives ppt. The most suitable reagents are triphenylmethylarsonium iodide, tetraphenylphosphonium chloride and tetraphenylarsonium chloride (**I**). Thus with **I**, 0·5 μg of Os can be detected in the presence of a 300-fold excess of Ru. *Procedure*—To the sample in 0·1 *N* HCl add a 1% aq. soln. of **I**. A cryst. ppt. indicates the presence of Os. Photomicrographs of the crystals are shown. J. P. STERN

524. **Determination of small quantities of platinum metals. I. New colorimetric method for osmium and ruthenium.** W. Geilmann and R. Neeb (Anorg.-anal. Inst., Univ. Mainz, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 96–107.—In the determination of Os and Ru with thiourea the colour formed is non-extractable and the two metals cannot be determined in the presence of each other. Therefore substituted thiourea and thiocarbazide derivatives were examined for the colorimetry of Os and Ru. For Os, NN′-di(2-tolyl)thiourea (**I**) and 1:4-diphenylthiosemicarbazide (**II**) are suggested, and for Ru, diphenylthiourea (**III**) and 2:4-diphenylthiosemicarbazide (**IV**). By the use of **I**, 15 to 175 μg of Os can be determined in HCl (6 to 9 *N*) with an accuracy within ± 3% without interference by SO_4^{2-} or ClO_4^-. Oxidising agents, SO_3^{2-}, Pd, Rh and Ru interfere, and Ir and Pt interfere slightly. *Procedure for Os* (*i*)—Acidify the soln. (1 to 12 μg of Os^{IV} per ml) until it is 6 *N* to HCl. Add 5% $SnCl_2$ in 6 *N* HCl (1 ml) and satd. methanolic **I** (1 ml) and heat at 100° for 15 min. Cool, extract with chloroform and compare the extinction (2-cm cell) at 490 mμ with a calibration curve. By the use of **II** in aq. $NaHCO_3$, 7 to 60 μg of Os is determined with an accuracy within ± 5%. Interference by SO_3^{2-}, NO_3^-, NaCl (> 0·02 g per ml), Pd (yellow colour) and Ru (> 10% of Os concn.) is noted. Addition of $SnCl_2$ obviates interference by Pt (green colour) and Rh (orange colour). *Procedure for Os* (*ii*)—Add satd. aq. $NaHCO_3$ (0·5 to 1 ml) to the weakly acid (≯ 0·05 *N*) Os soln. When CO_2 evolution has ceased, add satd. methanolic **II** (1 ml) and heat at 45° for 1 hr. Cool, add conc. HCl (2 to 3 ml) and $SnCl_2$ soln. (2 ml) and extract with chloroform (10 ml). Determine the extinction at 520 mμ. *Procedure for Ru* (*i*)—By the use of **III** in 6 *N* HCl, Ru (15 to 90 μg) is determined with an accuracy within ± 5% in the presence of a tenfold excess of Os. Small amounts of Pd, Ir, Rh, SO_4^{2-} and ClO_4^- do not interfere; Pt and oxidising agents interfere. Acidify the soln. (≯ 100 μg of Ru in 20 ml) with HCl until the acid is 5 to 6 *N*, add satd. methanolic **III** (1 ml) and heat at 80° for 30 min. Cool, extract with chloroform, and compare the extinction (2-cm cell) at 650 mμ with a calibration curve. *Procedure for Ru* (*ii*)—By the use of **IV** in 4 to 6*N* HCl, 2·5 to 25 μg of Ru can be determined to within ± 4% in the presence of a 20-fold excess of Os. Interference by Pd, Pt and Rh is serious only when they are present in fivefold excess; Ir, ClO_4^-, SO_4^{2-} and SO_3^{2-} do not interfere. Oxidising agents must be absent. Add to the soln. of Ru (≯ 30 μg in 15 ml) in 6 *N* HCl, saturated methanolic **IV** (1 ml) and heat at 100° for 10 to 15 min. Cool, extract with chloroform, and measure the extinction (2-cm cell) at 565 mμ. (See also *Anal. Abstr.*, 1957, **4**, 109.) J. P. STERN

525. **Determination of platinum in reforming catalyst by X-ray fluorescence.** E. L. Gunn (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1433–1436.—The sample, briquetted with an organic binder, is mounted in a specially designed holder and is examined in an X-ray fluorescence spectrometer, with a tungsten source, a lithium fluoride prism and counter detector. The Pt L_{β_1} line is measured at 32·2° and the concn. of Pt is deduced after deduction of background at 29·0°. Agreement with the spectrophotometric wet method is demonstrated and a precision of ± 0·006% for contents of Pt of 0·6% is claimed. Carbon, H_2O and Fe have no significant effect on the results. D. A. PANTONY

526. **Analysis of complex mixtures of elements resulting from the irradiation of fissile materials.** E. A. C. Crouch and G. B. Cook (A.E.R.E., Harwell, Berks.). *J. Inorg. Nucl. Chem.*, 1956, **2** (4), 223–228.—Radioactive isotopes of Rb, Sr, Y, Zr, Mo, Ru, Ag, Cd, Cs, Ce, Ba, La, Pr, Nd, Pm, Sm, Eu, U, Np and Pu are isolated from ≯ 250 mg of soil or rock (containing also Fe, Ca, Ti, Mg, Al, Si and Th), or from < 20 mg of neutron-irradiated U or Pu, by adding inactive carriers for as many of these elements as possible, followed by fusion of the dried mixture with 1 g of KOH, 1 g of K_2CO_3 and 2 g of KNO_3 in a nickel crucible for 2 hr. at 500° ± 10°. The melt is extracted with hot water in which Ru, Mo, Cs and Rb dissolve (soln. *A*); the residue is dissolved by fuming with HNO_3, $HClO_4$ and HF, then NH_3 gas is passed in, when Zr, U, Np, Pu, Fe, Al, Th and rare earths are pptd. (ppt. *A*) leaving Mg, Ba, Sr, Ca, Ag and Cd in solution. The latter elements, also those present in soln. *A*, are separated by semi-micro chemical methods. Ppt. *A* is treated to remove Al and Fe, then dissolved in 9 *N* HCl and passed through a column of anion-exchange resin: Pu, Np and U are absorbed and subsequently stripped successively by appropriate eluents. The Zr, Ti, Th and rare earths are separated on a further column of cation-exchange resin. The individual elements are purified by standard procedures (Coryell and Sugarman, N.N.E.S., Vol. IV–9, "Radiochemical Studies: The Fission Products," McGraw Hill, New York, 1951) to attain overall decontaminations of ≮ 10^4 from extraneous radioactivity. Recoveries of added carriers were > 40%; Np and Pu (10^{-12} g) were recovered in > 90% yield. E. N. JENKINS

See also Abstracts 567, 753, 754, 755, 756.

3.—ORGANIC ANALYSIS

527. **Standard [reference] chemicals in organic analysis: micro-determination of carbon and hydrogen.** L. J. Moelants (S.A. Photo-Produits Gevaert, Anvers). *Ind. Chim. Belge*, 1956, **21** (3), 207–220.—The use of reference chemicals in microchemical org. analysis for C and H is reviewed and, in a series of tables, the appropriate compounds for various combinations of elements are listed with their empirical formulae, m.p., mol. wt., and compositions in terms of elements present. (24 references.) S.C.I. ABSTR.

528. **Observations on carbon and hydrogen determination. I. The use of cupric oxide alone in the micro combustion apparatus.** Satoshi Mizukami, Tadayoshi Ieki and Nobu Morita (Shionogi Co. Ltd., Imafuku, Amagasaki, Hyogo Prefecture). *J. Pharm. Soc. Japan*, 1956, **76** (5), 601–604.—Since the lead dioxide is the greatest source of error in the micro-analysis of C and H, the use of a combustion tube containing only CuO was studied for the analysis of steroids. In the presence of halogens and S, the use of a silver-gauze roll suffices to fix those elements. The results for various compounds were compared with the calculated values; the standard deviations for C and H were $\pm$ 0·12 and $\pm$ 0·23%, respectively.

II; III. Main source of the blank value in the micro combustion apparatus. Satoshi Mizukami, Keiichi Miyahara and Nobu Morita. *Ibid.*, 1956, **76** (5), 553–559; 559–561.—The blank values for the determination of C and H with the apparatus described above are $\simeq$ 50 μg and $\simeq$ 30 μg, respectively. It was found that the source of the blank value is the rubber joints of the apparatus. It is also pointed out that wiping of the absorption tube with chamois leather brings about a significant fluctuation in the blank value. K. Saito

529. **The determination of halogens [in organic compounds] with [di]sodium diphenyl.** A. Sezerat, with Mme. Lanièce (Service de Recherches Rousse-Uclaf, Paris-Romainville). *Ann. Pharm. Franç.*, 1955, **13** (12), 745–748.—Organic halogen is mineralised by treatment with disodium diphenyl and determined argentimetrically. *Procedure*—The sample ($\simeq 2 \times 10^{-3}$ mole) is dissolved in exactly 20 ml of anhyd. toluene and disodium diphenyl reagent is added until a deep-green colour persists. (This reagent is prepared by pulverising Na under boiling toluene and nitrogen and, after cooling, adding 1:2-dimethoxyethane and diphenyl while keeping the temp. $< 50°$; it may be stored at 0°.) After 5 min., 20 ml of water is added to destroy the reagent and the org. layer is extracted three times with 3 *N* HNO_3. To the collected aq. phases is added 25 ml of 0·1 *N* $AgNO_3$ and the excess is determined by titration with NH_4SCN solution (AgI must first be filtered off). In some cases a brown colour is extracted into the aq. phase and this colour is destroyed with $KMnO_4$, excess of which is removed with H_2O_2. Among the results quoted are those for the volatile allyl bromide.
E. J. H. Birch

530. **Micro-determination of fluorine in organic compounds by means of high-frequency titration.** P. Monand (Centre de Recherches, Cie de Saint-Gobain, Antony, France). *Bull. Soc. Chim. France*, 1956, (4), 704–707.—The sample, containing $\simeq$ 3 mg of F, is burned in a stream of O (10 ml per min.) and the gases are passed through a quartz tube at 1150° containing a platinum catalyst where SiF_4 is formed. The gases then pass to a solution of Na acetate where NaF is formed. This is then titrated in the same vessel with 0·02 *N* La or Sr acetate by high-frequency titration. Chlorine can interfere but may be quantitatively retained by (and weighed on) silver - pumice. The precision is $\pm$ 0·2%.
E. J. H. Birch

531. **High-frequency titrations of some organic functional groups.** R. Hara and P. W. West (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1956, **15** (2), 193–200.—When 0·001 *M* aq. soln. of malonic, tartaric and phthalic acids are titrated with 0·0278 *M* NaOH by the high-frequency method only the first acidic H can be titrated in each acid. The limiting dissociation constant for acids titratable by this method is $\simeq 10^{-3}$; in pyridine the limit is $\simeq 10^{-5}$. Lactic, tartaric, succinic, citric, formic and propionic acids are titrated in pyridine with 0·09 *M* alcoholic KOH; tartaric and citric acids then behave as dibasic acids and succinic acid behaves as a monobasic acid. Brucine, *o*-phenanthroline, diethylamine, *p*-toluidine, 2-naphthylamine and *o*-phenylenediamine are titrated in acetic acid with a standard soln. of $HClO_4$ in acetic acid. For this method the limiting K_b is $\simeq 10^{-10}$. Benzoin α-oxime is determined by acidimetric titration after adding Cu^{2+} to form the copper complex; salicylaldoxime is treated similarly and nitroso-R salt is titrated after adding Co^{2+}.
W. C. Johnson

532. **The semi-micro determination of methoxyl.** P. O. Bethge and O. T. Carlson (Swedish Forest Prod. Res. Lab., Stockholm, Sweden). *Anal. Chim. Acta*, 1956, **15** (3), 279–283.—The various stages in the standard Zeisel determination of methoxyl groups are discussed critically, and an improved apparatus—a modification of Gran's (*Svensk Papp.-Tidn.*, 1952, **55**, 255)—is described and illustrated. For aiding dissolution of the sample, the mixtures recommended by Belcher *et al.* (*cf. Anal. Abstr.*, 1955, **2**, 3380) and Kirsten and Ehrlich-Rogozinsky (*Anal. Abstr.*, 1955, **2**, 3080) are equally satisfactory, although the latter mixture (one-phase only) is preferred as it can be added initially to the HI in the cold. Aqueous 5% $CdSO_4$ is the preferred wash soln.
W. J. Baker

533. **Micro-determination of the acetyl group. I. Examination of the iodimetric determination.** Satoshi Mizukami, Tadayoshi Ieki and Chieko Koyama (Shionogi & Co. Ltd., Imafuku, Amagasaki, Hyogo Prefecture). *J. Pharm. Soc. Japan*, 1956, **76** (4), 465–467.—The iodimetric titration of a micro amount of acetyl groups described by Friedlich (*Biochem. Z.*, 1932, **251**, 432) was modified by titrating the excess of 0·01 *N* $Na_2S_2O_3$ added to the sample distillate. The effect of SO_2 produced by the decomposition of toluene-*p*-sulphonic acid (**I**) is eliminated as follows. The sample is decomposed with **I** (25%, 2 ml) and distilled into an ice-cooled receiver containing KI (1·5 g) and 0·01 *N* iodine soln. (5 ml). After the distillation is completed (for N-acetyl, 3 hr., O-acetyl, 1 hr.), the distillate is titrated with 0·01 *N* $Na_2S_2O_3$ (indicator 1% starch soln.) (*A* ml). The product is treated with 4% KIO_3 (2 ml) and a known excess of 0·01 *N* $Na_2S_2O_3$ and titrated with 0·01 *N* iodine soln. (*B* ml). A mixture of KI (1·5 g), 0·01 *N* iodine soln. (5 ml) and one drop of 10% acetic acid is titrated with 0·01 *N* $Na_2S_2O_3$ (*C* ml). The amount of acetyl groups is calculated from $[B - 2(C - A)]$ with an error $< 0·5\%$.

II. The use of cation-exchange resin. Satoshi Mizukami and Tadayoshi Ieki. *Ibid.*, 1956, **76** (4), 467–468.—The cation-exchange resin Amberlite IR-120 is satisfactorily used for a micro-determination of acetyl groups. The sample (4 to 6 mg) is refluxed with *N* NaOH (2 ml) and the product is passed through a column of the resin. The eluate and the washings are treated with KI (1·5 g), KIO_3 (4%, 2 ml) and an excess of 0·01 *N* $Na_2S_2O_3$; the excess of $Na_2S_2O_3$ is back-titrated with 0·01 *N* iodine.
K. Saito

534. **Qualitative gas-chromatographic analysis using two columns of different characteristics.** J. S. Lewis, H. W. Patton and W. I. Kaye (Tennessee Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1370–1373.—Elution times of known volatile compounds from two gas - liquid partition columns having different characteristics were plotted logarithmically and each compound studied had a definite location on the plot. The columns used were packed with Celite 545, which was impregnated with tricresyl phosphate in one column and Cenco Hyvac oil (a vacuum-pump oil) in the other. The method was simple and effective for the identification of alkanes, cycloalkanes, esters, aldehydes, ketones and alcohols. The points for the members of a given homologous series lay on a smooth curve which was almost linear, and consecutive members were approximately equally spaced. G. P. Cook

535. **Determination of dissolved oxygen in hydrocarbons.** A. B. McKeown and R. R. Hibbard (Lewis Flight Propulsion Lab., Nat. Advisory Committee for Aeronautics, Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1490–1492.—The method is a modification of the Winkler procedure. Fuels are shaken with an alkaline suspension of $Mn(OH)_2$ and $Fe(OH)_2$ and the system is acidified; Fe^{3+} are formed in proportion to the oxygen dissolved in the hydrocarbon and are determined iodimetrically. Thiols do not appreciably affect the result, but peroxides interfere. A correction factor for peroxides is proposed. The accuracy is probably within $\pm$ 10%. G. P. Cook

536. **Determination of acetylenic compounds via hydration.** S. Siggia (General Aniline & Film Corp., Easton, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1481–1483.—The method is based on the hydration of the acetylenic triple-bond in strongly acidic medium with a mercuric catalyst. The acetone formed is measured by the use of hydroxylamine hydrochloride. The precision and accuracy are generally within $\pm$ 2·0% depending on the compound analysed. Ketones, not readily determined by oximation, are measured by pptn. with 2:4-dinitrophenylhydrazine. G. P. Cook

537. **Sulphonation and sulpho acids of acidophobic compounds. XXV. Use of dioxan - sulphur trioxide for determination [of active hydrogen atoms] of mono- and poly-hydroxy compounds.** A. P. Terent'ev and N. B. Kupletskaya (Moscow State Univ.). *Zhur. Obshch. Khim.*, 1956, **26** (2), 451–454.—Air is bubbled successively through 60% oleum and anhyd. dioxan, until a ppt. of dioxan - sulphur trioxide, $O(CH_2CH_2)_2O{\cdot}SO_3$, appears. Sufficient dioxan is added to dissolve the ppt., giving a 1·5 to 2 *N* solution, to 1 or 2 ml of which is added a sample of substance (*s*) under analysis (*s* = 0·02 to 0·05 g), followed after 2 or 3 min. by 10 ml of water and a few drops of indicator (Congo red, bromophenol blue or methyl orange), and the solution is titrated with *x N* Na_2CO_3; the active hydrogen content per 100 g of substance is given by $H = (a - b)x/10s$, where *a* and *b* are ml of *x N* Na_2CO_3 used for titration of the reagent in the presence and absence of the substance, respectively. The experimental error is $\simeq$ 2 or 3% for *prim.*- *sec.*- and *tert.*-OH groups of mono- and polyhydric alcohols, sugars, and ketoximes; the method cannot be applied to phenols or aldoximes, or in their presence. Esters, cyanides, amides and nitro compounds do not interfere. R. Truscoe

538. **Colour reactions of aldehydes and ketones with vanillin in alkaline medium.** V. E. Levine and M. Taterka (Creighton Univ. School of Med., Omaha, Neb., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (3), 237–245.—The specificity of colour reactions between vanillin (1% aq. soln.) and various aldehydes and ketones in the presence of 5 to 10 *N* NaOH has been studied. The results are listed. Where reaction occurs, yellow, brown or red colorations are obtained, the colour and intensity depending on the constitution and concn. of the aldehyde or ketone. Max. sensitivity is attained with cyclic and aliphatic ketones, especially those containing methyl groups (acetone, diethyl ketone), but the reactivity decreases with increasing chain-length in the radical (methyl propyl ketone, undecylic ketone). Ketones with one aryl group are only slightly reactive; if both radicals are aryl groups the reaction is negative (benzophenone, di-*p*-tolyl ketone). Aliphatic aldehydes are more reactive than aromatic aldehydes. Some ketonic and hydroxy acids give positive reactions. W. J. Baker

539. **The separation of organic acids from vegetable matter by dispersion chromatography on paper and silica-gel columns.** R. Ya. Shkol'nik. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1955, **6**, 502–508; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,608.—The organic acids are extracted by ether from a suspension of the dry vegetable matter in 4 *N* H_2SO_4 with asbestos. The acids are then extracted from the ether layer with water. For the qualitative identification of the acids, paper chromatography is used, with the following mixtures as dispersing solvents—ethanol - aq. NH_3 - H_2O (90:5:5); 30 g of phenol, 10 ml of water and 0·4 ml of 90% formic acid; $CHCl_3$ - ethanol - 90% formic acid (2:1:2); and *n*-butanol - formic acid - H_2O (18:2:9). Best results are obtained with the last solvent. The R_F values for the acids are—oxalic 0·09, acetic 0·21, citric 0·31, malic 0·46, glycollic 0·56, succinic 0·68, and fumaric 0·72. For the quant. determination, chromatography on columns of silica gel is used. For close values of R_F, the separation is carried out not from aq. soln., but from soln. in a mixture of *n*-butanol and $CHCl_3$ (35:65). C. D. Kopkin

540. **Determination of formic, acetic and propionic acids in their neutral and basic salts of copper, pure or in solution.** J. Gauthier (Fac. des Sci., Lyons, France). *Bull. Soc. Chim. France*, 1956, (4), 657–660.—The acids are distilled from H_3PO_4 solution and titrated with *N* NaOH. *Procedure*—The salt is heated with 10 ml of 85% H_3PO_4 in a long-necked thin-walled vessel connected to a condenser dipping under water. The water in the vessel contains mixed phenolphthalein - bromothymol blue indicators and is kept just alkaline by addition of *N* NaOH from a burette. When the contents of the flask have evaporated to dryness (but not solidity), the water is allowed to suck back somewhat to rinse the condenser and, after addition of more water, the evaporation to dryness is repeated three times more, and the total quantity of *N* NaOH is taken as the titre of acetic acid. The formate (formic acid forms a negative azeotrope) is similarly determined, but the method is modified by a previous precipitation of Cu^{2+}, either with Zn or as CuO with NaOH. The propionate (propionic acid forms a positive azeotrope) is determined similarly. Comment is made on the possibility of attack on the glass of the flask by the H_3PO_4 with liberation

of Cl from the glass. This attack is found to be more severe with thick-walled vessels.

E. J. H. BIRCH

541. **Determination of di- and tri-chloroacetic acids in chloroacetic acid.** N. Bellen and M. Jurowska-Wernerowa (Zakład Anal., Inst. Chem. Ogólnej). *Przem. Chem.*, 1955, **11**, 526–527.—Di- and tri-chloroacetic acids react with sodium hydroxide to give glyoxylic acid and chloroform which may be then determined colorimetrically by the use of naphthoresorcinol and resorcinol, respectively. The colours so formed were evaluated by comparison against those given by mixtures containing various proportions of cobalt and iron chlorides. Chloroacetic acid does not interfere with these tests. The method is considered suitable for qual. and semi-quant. determination of di- and tri-chloroacetic acids in the chloro acid. (*i*) *Dichloroacetic acid*—Dissolve the chloroacetic acid sample (containing the free acid or its salts) (≡ 0·05 to 0·5 mg of dichloroacetic acid) in water (0·5 ml), add 30% NaOH (1·3 ml) and heat to boiling point (1 min.). Cool, add aq. 1% naphthoresorcinol soln. (4 drops) and conc. HCl (3 ml). Heat to boiling point, dilute with water (5 ml) and cool. Add benzene (5 ml) and shake for 2 min. Determine the intensity of the pink colour in the benzene layer, which is proportional to the concn. of dichloroacetic acid. (*ii*) *Trichloroacetic acid*—Dissolve the chloroacetic acid sample (≡ 0·2 to 2 mg of trichloroacetic acid) in water (2 ml), add 10% resorcinol soln. (2 ml) and 30% aq. NaOH (3 ml) and boil for 1 min. Determine immediately the intensity of the red colour, which is proportional to the concn. of trichloroacetic acid.

K. F. SOREK

542. **Paper chromatography with continuous change in solvent composition. I. Separation of fatty acids.** F. Franks (Brit. Launderers' Res. Ass., Hillview Gardens, London). *Analyst*, 1956, **81**, 384–390.—A simple apparatus is described and illustrated in which paper chromatography is carried out with a solvent that changes continuously in composition in an exponential manner. Closely similar compounds, *e.g.*, members of a homologous series, can thus be separated on a short paper strip without diffusiveness of zones. For the separation of mixtures of long-chain fatty acids, the original solvent is 50% acetic acid, and the component introduced under a constant head is glacial acetic acid. The paper is first impregnated with liquid paraffin and the mixture of fatty acids is applied to it. The paper, which is of a specified shape, is placed horizontally with its wick dipping into the solvent and a similar reference strip with specified amounts of the appropriate fatty acids is placed alongside. The composition of the solvent is then varied continuously. The dried chromatograms are washed with water, immersed in 1% ammoniacal $AgNO_3$ soln. and washed free from soluble silver salt. They are then treated with dil. Na_2S soln. until the spots of Ag_2S attain their max. colour. The sample chromatogram is then compared with the standard. The method has been applied to the separation of mixtures of fatty acids obtained from acetone extracts of laundered articles.

II. Separation of surface-active agents. F. Franks. *Ibid.*, 1956, **81**, 390–393.—The method and apparatus described in Part I are applied to mixtures of surface-active agents and commercial detergents. The paper is impregnated with cetyl alcohol and a soln. of the mixture of alkyl sulphates (up to 200 μg) is applied to it. The mobile solvent is 50% aq. ethanol saturated with cetyl alcohol and it is continuously diluted with water in the apparatus. The chromatogram is immersed in cupric acetate soln., dried, immersed in rhodamine-B soln., dried, and examined in u.v. light. The zones appear purple on a fluorescent pink background. Results show that a resolution of detergents into pure compounds is feasible. Since pure reference compounds are not readily available, it has not yet been possible to identify the resolved components of the commercial detergents used. A. O. JONES

543. **Paper-chromatographic separation of the N-acyl-NN′-di-*p*-dimethylaminophenylurea derivatives of the fatty acids.** M. R. Tulus and O. Y. Izgi (Inst. Anal. Chem. and Toxicol. Pharm. Sch. Univ. of Istanbul, Turkey). *Arch. Pharm., Berlin*, 1956, **289** (3), 127–132.—The ureide derivatives of the C_4 to C_{20} saturated fatty acids and some unsaturated members are separated by paper chromatography. The ureide of stearic acid is prepared by dissolving 56·8 mg of stearic acid in 5 ml of dry ether to which is added 5 ml of an ethereal soln. of carbodi-*p*-dimethylaminophenylimide, and the mixture is heated under reflux on a water bath for 2 hr. Crystallisation occurs on cooling (yield 72·6% of theoretical). A soln. containing 0·5-μl quantities of a 0·5% soln. of the ureide in ethyl acetate is applied to an ascending paper chromatographic strip, previously impregnated with a petroleum jelly soln. (80 g in 800 ml of toluene, allowing solvent to evaporate). For the saturated C_{12} to C_{20} acids and certain unsaturated acids, water - acetic acid - dioxan (33:52:15) has been used, whereas for the saturated C_4 to C_{10} acids, water - acetic acid - ethyl acetate (65:22·5:12·5) is employed. After separation, the dried strip is sprayed with 7% $NaNO_2$ - *N* HCl (1:1) and the R_F values are determined.

G. R. WHALLEY

544. **Infra-red identification of fumarates and maleates.** W. L. Walton and R. B. Hughes (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1388–1391.—Fumarates give a series of absorptions at 7·7, 7·9, 8·5, 8·6, 10·2, 12·9 and 15 μ which are relatively constant in wavelength and intensity. The maleates have peaks of constant wavelength at 7·75, 8·00, 8·20 and 8·60 μ. The 8·20-μ peak is of value for the measurement of maleates in the presence of fumarates.

G. P. COOK

545. **Determination of maleic hydrazide. II. Polarographic determination of maleic hydrazide.** Tsugio Takeuchi, Naruhito Yokouchi and Kiyoshi Onoda (Dept. of Applied Chem., Faculty of Eng., Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1956, **5** (7), 399–403.—The polarographic reduction of maleic hydrazide (**I**) was studied in buffer soln. of various pH values in the presence of diethanolamine (**II**). The reduction wave is a distinctive one-step wave at pH 3 and 7, irrespective of the amount of **II**, the height being proportional to the concn. of **I**. Hydrazine fails to give a reduction wave under the given conditions, whilst the wave of maleic acid (**III**) (> 1% in **I**) at − 1·84 V *vs.* the normal calomel electrode coincides with that of **I**; **III** gives a less distinctive wave at − 1·54 V, from which the wave height of **III** at − 1·84 V is roughly estimated. The sodium salt of **I** also shows a reduction wave similar to that of **I**. This method is applied to the analysis of agricultural chemicals; the interference of **III** (≃ 0·1% in **I**) is negligible.

III. Ultra-violet spectrophotometric determination. Tsugio Takeuchi, Motohisa Furusawa and Kiyoshi Onoda. *Ibid.*, 1956, **5** (7), 404–407.—An aq. soln. of **I** has a max. absorption at 302 mμ, the extinction coeff. being proportional to concn. (< 25 μg per ml). In the presence of **II**, the max. absorption is shifted to 325 mμ; on the addition of 0·0015 to 0·15 *M* H_2SO_4, however, the absorption appears at 302 mμ, and Beer's law is obeyed. Hydrazine fails to give an absorption under the given conditions. **III** shows marked absorption at 330 mμ, but the amount in industrial **I** is so small that its absorption is negligible. K. SAITO

546. **Determination of succinic, maleic and fumaric acids in a mixture.** Z. Bellen and B. Sękowska (Zadład Anal. Inst. Chem. Ogólnej). *Przem. Chem.*, 1955, **11**, 523–526.—A mixture of succinic, maleic and fumaric acids is produced during the catalytic hydrogenation of sodium maleate. Several existing methods for the determination of these acids based on their pptn. as heavy-metal salts were found to be unsatisfactory. A satisfactory method was developed which consists in determining the total amount of the three acids by potentiometric titration of their sodium salts with $HClO_4$ in glacial acetic acid and in determining maleic and fumaric acids by polarography. The succinic acid content is then calculated by difference. (*i*) *Total acids*—Dissolve the sodium or potassium salts (≡ 1 g of the acids) in a little water. Neutralise the soln. to phenolphthalein with 0·2 *N* NaOH or HCl. Dilute the soln. to 100 ml with water. Pipette 10 ml of the soln. into a 100-ml beaker and evaporate to dryness on a water bath. Dissolve the residue in glacial acetic acid (40 ml), and titrate potentiometrically with 0·1 *N* $HClO_4$ in glacial acetic acid. (*ii*) *Maleic and fumaric acids*—Weigh the sample (≡ 3 to 25 mg of maleic and fumaric acids) into a 100-ml flask, dissolve in about 20 ml of water and neutralise to phenolphthalein. Add 70 ml of a buffer soln. (53·5 g of NH_4Cl in 1 litre of water and conc. aq. NH_3 to give a pH of 8·2) and dilute to 100 ml with water. Examine polarographically. $E_{\frac{1}{2}}$ *vs.* the S.C.E. for maleic acid = 1·42 *V*, and for fumaric acid = 1·62 V. (*iii*) *Maleic acid* (*or total unsaturated acids*)—Weigh the sample (≡ 0·3 g of maleic anhydride) into a 500-ml flask, dissolve in water and dilute to 500 ml. Pipette 25 ml of the soln. into a 200-ml flask, add 20 ml of 0·1 *N* $KMnO_4$ and conc. H_2SO_4 (0·5 ml) and set aside for 30 min. Add 5% KI soln. (10 ml) and titrate the liberated iodine with 0·1 *N* $Na_2S_2O_3$ in the usual way.
K. F. SPOREK

547. **The preparation and development of paper chromatograms of carbohydrates.** E. K. Surykina. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1955, **6**, 483–485; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,442.—To develop the spots due to carbohydrates on chromatograms, use is made of the ability of carbohydrates to caramelise on heating. In the experiments, thick filter-paper was used, in sheets 50 cm × 50 cm or 100 cm × 60 cm. To obtain chromatograms by the vertical adsorption method, the paper is placed in special glass spiral holders. Phenol saturated with water and containing some ethanol is used as solvent. The chromatograms are dried in the air for 2 to 5 days to remove as much phenol as possible, and then placed in a thermostat at 150° for 2 to 5 hr. The sensitivity of the reaction is 3 × 10^{-5} mg.
C. D. KOPKIN

548. **The analysis of the hydrolysis products of inulin by paper chromatography.** I. R. Rominskiĭ. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1955, **6**, 492–497; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,443.—Inulin is completely hydrolysed in the presence of 0·14 *N* HCl at 85° in 35 min. Hydrolysis in the presence of a cation-exchange resin (Espatit I of average grain-size 0·45 mm) took 4 hr. at 90° with stirring. The hydrolysis products were studied by vertical adsorption paper-chromatography on paper strips 10 to 15 cm × 50 cm. The following mixtures were used as solvents—phenol - H_2O (8:2); ethyl acetate - pyridine - water (2:1:2) and *n*-butanol - pyridine - water (3:2:1). An alcoholic soln. of 1-naphthol with H_3PO_4 and an alcoholic soln. of benzidine with acetic acid were used as developers. The product of the hydrolysis of inulin by *N* HCl and H_2SO_4 contains five carbohydrates—glucose, fructose, and three dianhydrides of difructose.
C. D. KOPKIN

549. **Comparative determinations of cellulose.** K. Stolk (Rijkslandbouwproefstation Hoorn, Holland). *Chem. Weekbl.*, 1956, **52** (37), 682–687.—A critical assessment is made of a number of recognised methods for the determination of cellulose; these have been tested on S. & S. filter-paper No. 589 and No. 292 as well as on a sample of air-dry autumn grass. The methods tested were those of (*i*) Norman and Jenkins (*Biochem. J.*, 1933, **27**, 818), (*ii*) Crampton and Maynard (*J. Nutrition*, 1938, **15**, 383), (*iii*) Viles and Silverman (*Anal. Chem.*, 1949, **21**, 950), and (*iv*) Weender, as modified by Holdefleisz, and by Campen (*Landbouwk. Tijdschr.*, 1949, **61**, 785). A few minor improvements were made in carrying out methods (*i*) and (*ii*). In method (*iii*) the requisite temp. conditions for hydrolysis were obtained by heating the material with 60% (w/v) H_2SO_4 immersed in a water bath for 5 min. at 95° and for 10 min. at 90°. Method (*i*) was not considered to be suitable for a series of technical analyses; it gave higher results than the other methods but the mean deviation of methods (*i*), (*ii*) and (*iv*) did not show much variation, indicating that their reliability was roughly equivalent. Method (*iii*) gave the lowest result of all for grass, but the values found were closely reproducible. Methods (*ii*), (*iii*) and (*iv*) are suitable for a series of determinations. P. HAAS

550. **Infra-red determination of the mixed vapours of carbon tetrachloride and ethylene dichloride [1:2-dichloroethane] in air.** H. K. Heseltine (Pest Infestation Lab., D.S.I.R., Slough, England). *Chem. & Ind.*, 1956, (35), 910–911.—The method is applicable to the determination of concn. of fumigants in air. *cyclo*Hexane is introduced into a sampling flask (illustrated), which is then immersed in a freezing mixture to allow the *cyclo*hexane to solidify. The flask is then evacuated to ≃ 1 mm (Hg); negligible loss of *cyclo*hexane occurs under these conditions. The flask is set aside until the *cyclo*hexane is liquid again, and the sample of air containing a mixture of CCl_4 and 1:2-dichloroethane is drawn in, and shaken gently. The *cyclo*hexane is poured out, and an aliquot is transferred to a variable-path rock-salt cell for infra-red analysis in a double-beam spectrometer. Concn. of 0·4 to 20 mg of each component per ml (equiv. to concn. in air of 10 to 500 mg per litre) have been determined, with a max. error of 5% on the expected figures. The sample may be retained in the flask for several days before analysis.
O. M. WHITTON

551. **Colorimetric determination of nitromethane in the presence of other nitroparaffins.** L. R. Jones and J. A. Riddick (Commercial Solvents Corp., Terre Haute, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1493–1495.—Nitromethane reacts with Na 1:2-naphthaquinone-4-sulphonate in alkaline soln. to form a violet complex. This is extracted into *iso*amyl alcohol and the extinction is measured at 585 mμ. Beer's law is obeyed in the range 5 to 30 μg and the method has an accuracy within ± 2% and a precision within ± 1%. The reaction is specific for nitromethane in the presence of other nitroparaffins, some of which, when present in excessive quantities, inhibit the colour formed. In this event the nitromethane is first separated by azeotropic distillation with methanol.

G. P. Cook

552. **The colorimetric determination of secondary [alkyl] amines.** C. F. Cullis and D. J. Waddington (Imperial Coll. of Science and Technology, London). *Anal. Chim. Acta*, 1956, **15** (2), 158–163.—The violet - blue colour that is produced when secondary alkylamines react with sodium nitroprusside and acetaldehyde (Feigl and Anger, *Mikrochim. Acta*, 1937, **1**, 138) is used as the basis of a quant. method for secondary amines in the presence of primary and tertiary amines and NH_3. *Procedure*—Prepare a buffer soln. of pH 9·8 by dissolving 9·53 g of $Na_2B_4O_7.10H_2O$ and 5·30 g of Na_2CO_3 in sufficient water to produce 1 litre. To 20 ml of this soln. add 5 ml of a soln. of acetaldehyde (10% v/v) and sodium nitroprusside (1% w/v); add 5 ml of the test soln. and compare the extinction with that of a blank containing 5 ml of water in place of the test soln. For dimethylamine $\lambda_{max.} = 565$ mμ; its determination is studied in concn. up to 0·003 *M*; the extinction does not reach a maximum within a reasonable time and a standard time interval (20 min.) is therefore adopted. Diethylamine yields a less sensitive reaction but is determined in a similar manner. Relevant characteristics are also given for di-*n*-propyl-, di-*n*-butyl-, di-*n*-amyl- and di-*iso*butyl-amine. Secondary amines with N attached to CH groups give no appreciable colour.

W. C. Johnson

553. **The chromatography of some hydrazine derivatives on paper.** R. L. Hinman (State Univ. of Iowa, Iowa City, U.S.A.). *Anal. Chim. Acta*, 1956, **15** (2), 125–128.—The R_F values have been determined for a number of acyl- and alkyl-hydrazines. The circular and the strip (ascending) methods of paper chromatography are used. For the acyl derivatives the solvent is the upper layer from a mixture of *iso*amyl alcohol, acetic acid and water (10:1·5:10, by vol.). For the alkyl derivatives the solvent is the upper layer from a mixture of *n*-butanol, acetic acid and water (4:1:5, by vol.). Ammoniacal $AgNO_3$, ninhydrin soln. and Ehrlich's reagent are used to reveal the spots, but the last is the most generally useful. W. C. Johnson

554. **Spectrophotometric determination of microgram quantities of disodium dihydrogen ethylenediaminetetra-acetate.** O. Menis, H. P. House and I. B. Rubin (Anal. Chem. Div., Oak Ridge Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1439–1441.—The EDTA (disodium salt) soln. is allowed to react with an excess of Cu^{2+} at pH 11 (Na_2HPO_4 buffer) and the absorption is measured at 250 mμ with respect to a Cu^{2+} - Na_2HPO_4 blank. The effects of concn. of buffer and Cu^{2+}, temperature and standing time are investigated. Interference is caused by Ni^{2+}, Co^{2+} and CrO_4^{2-}, but not by ions that form less stable complexes with EDTA than Cu^{2+}. In the range 125 to 1500 μg, the precision is 8 to 2%.

D. A. Pantony

555. **Fearon's amidine - pentacyanoamminoferrate reaction in paper chromatography [of guanidine derivatives].** P. H. List (Inst. für Pharm. und Lebensmittelchemie der Univ., Wurzburg, Germany). *Hoppe-Seyl. Z.*, 1956, **303** (1–2), 27–29.—When the pentacyanoamminoferrate reagent of Fearon (*Analyst*, 1946, **71**, 562) is used for the detection of guanidine derivatives on paper chromatograms that have been developed in acid solvent mixtures, no colours are obtained. If a strongly alkaline soln. is used, then colours varying from orange with guanidine to violet with creatine are obtained for a number of derivatives. The reaction is more rapid when a small quantity of H_2O_2 is added as oxidising agent. To prepare the pentacyanoamminoferrate, dissolve recryst. sodium nitrosoferricyanide (10 g) in conc. aq. NH_3 (40 ml) and allow to stand at 0° until no red colour is obtained when a drop of the mixture is added to a soln. of creatinine in *N* Na_2CO_3. Filter and add absolute ethanol to the filtrate until no further ppt. forms. Filter off the ppt., wash with absolute ethanol and dry *in vacuo* over H_2SO_4. When kept dark and dry the solid is stable. To prepare the reagent, mix 20% NaOH soln. (5 ml), 1% pentacyanoamminoferrate soln. (15 ml) and conc. H_2O_2 (1 drop). This mixture is stable for 24 hr. F. Powell

556. **Colorimetric determination of carvone with ethyl 3:5-dinitrobenzoate.** D. H. E. Tattje (Lab. Farmacog., Galen. Farm. en Receptuur der Rijksuniv. Groningen, Holland). *Pharm. Weekbl.*, 1956, **91** (20), 733–736.—An ethanolic soln. (4 ml) containing ≮ 1 mg of carvone per ml is mixed with 5 ml of a 2% (w/v) soln. of ethyl 3:5-dinitrobenzoate in methanol; 1 ml of 0·70 *N* NaOH is then added. After exactly 3·5 min., the colour intensity is measured in a 1-cm cell at 5375 A against a freshly prepared control soln. of a mixture of 4 ml of ethanol, 5 ml of reagent and 1 ml of 0·70 *N* NaOH, at 20°. The calibration curve for a concn. of from 5 to 40 mg of carvone per 10 ml final vol. is rectilinear. $E^{1\%}_{1\,cm} = 2{\cdot}55$.

P. Haas

557. **The standardisation of alumina for chromatographic separation of polycyclic aromatic hydrocarbons.** A. J. Lindsey, E. Pash and J. R. Stanbury (Sir John Cass Coll., London, England). *Anal. Chim. Acta*, 1956, **15** (3), 291–293.—Alumina for the column-chromatographic separation of microgram amounts of aromatic polycyclic hydrocarbons can be prepared for use by equilibrating it for ≮ 48 hr. with water vapour from aq. 70% w/v H_2SO_4 in a desiccator. The standardisation procedure described is based on that of Wedgwood *et al.* (*Analyst*, 1953, **78**, 170), *cyclo*hexane being used as the eluting soln. In this way, ≃ 2 mg of acenaphthylene, anthracene, fluoranthene and perylene in 100 ml of solvent can be separated, and the u.v. absorption peaks and extinctions of the successive eluates can be determined. W. J. Baker

558. **Identification of some polynuclear aromatic hydrocarbons in the atmosphere.** V. C. Shore and M. Katz (Defence Res. Chem. Lab., Ottawa, Canada). *Anal. Chem.*, 1956, **28** (9), 1399–1402.—Samples of dust were collected on fibre-glass filters and the separation of single aromatic hydrocarbons from interfering compounds was effected by solvent

extraction and chromatographic adsorption analysis. The hydrocarbons were identified by u.v. absorption. The polynuclear aromatics thus identified were pyrene, fluoranthene, 1:2-benzanthracene, chrysene and 1:2-benzopyrene. G. P. Cook

559. **Specific colour reactions of certain phenols and utilisation of these reactions for the estimation of 2-naphthol in 1-naphthol and for the different constituents of technical mixtures of *m*- and *p*-cresols.** L. Nicolas and R. Burel (Cie Française de Matières Colorantes, Usine d'Oissel, France). *Chim. Anal.*, 1956, **38** (9), 316–321.—The determination of 2-naphthol in 1-naphthol depends on the fact that 2-nitroso-1-naphthol is pptd. when the mixture is treated with HNO_2. *Procedure*—A methanolic soln. of technical 1-naphthol (20 ml; 1%) is pipetted into a 100-ml calibrated flask. Water (60 ml) at 10° is added, followed by *N* $NaNO_2$ (1·4 ml) and 15% HCl (15 ml). The vol. is made up to 100 ml with water. The soln. is transferred to a 300-ml conical flask and rapidly cooled to between 8° and 10° in an ice-bath. The 2-nitroso-1-naphthol is filtered off and to the filtrate (50 ml) are added methanol (10 ml) and *N* $NaNO_2$ (2 ml) and the vol. is made up to 100 ml with water. After 10 min. a red colour develops, which is measured in a colorimeter. The determination of *p*-, *m*- and *o*-cresols and phenol in mixtures depends on similar colour reactions. *Procedure*—(*i*) p-*Cresol*—A soln. of the crude cresol [20 ml; 1%(w/v)] is introduced into a 100-ml calibrated flask. To this soln. are added 1-nitroso-2-naphthol [4 ml; 1% (w/v) soln. in glacial acetic acid], water (50 ml) and conc. HCl (5 ml), followed rapidly by *N* $NaNO_2$ (2 ml). The colour takes 2 to 3 hr. to develop. Excess of the reagent and the nitronaphthol formed are extracted with benzene (2 × 50 ml) before the colour is measured. (*ii*) m-*Cresol*—A soln. of the sample [10 ml; 1% (w/v) soln. in glacial acetic acid] is pipetted into a 125-ml flask. Water (25 ml) is added and the flask is placed in an ice-bath for 15 min. Conc. HNO_3 (5 ml) is added rapidly and the flask is set aside for 1 hr. at room temp. Conc. HCl (20 ml) is added and the soln. is extracted with benzene (2 × 50 ml). The coloured soln. is filtered and the colour is compared in a colorimeter with the colours of mixtures of known composition. (*iii*) o-*Cresol and phenol*—The sample (0·5 g) in a 50-ml flask is treated with oxalic acid soln. [15 ml; 50 g dissolved in 1 litre of 80% (w/v) H_2SO_4]. The flask is heated on a water bath at 50° for 1 hr., with shaking, then on a boiling-water bath for 5 min. The absorption of the cooled soln. is measured, with green and with blue filters, and the proportion of phenol is calculated by comparison with standard mixtures. C. A. Slater

560. **Induced reactions in cerimetry. I. [Determination of quinol.]** G. Gopala Rao and T. P. Sastri (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **152** (5), 351–355 (in English).—Oxalic acid interferes in the determination of quinol with $Ce(SO_4)_2$, presumably owing to an induced reaction in which oxalic acid acts as acceptor and quinol as inductor. This interference is independent of the internal indicator, but is nearly suppressed by H_3PO_4; it is eliminated by NaF. Citric, tartaric, malic and lactic acids, glucose and glycerol do not interfere. J. P. Stern

561. **The proximate analysis of cinnamaldehyde mono-nitration products.** W. Davey and J. R. Gwilt (Acton Tech. Coll., London). *J. Appl. Chem.*, 1956, **6** (4), 142–145.—The difficulties involved in estimating the various functional groups in nitrated cinnamaldehyde are discussed. A method that gives an overall accuracy within ± 5% is described. *Procedure*—The sample is refluxed with a suspension of $Mg(OH)_2$ for 15 min. and, after addition of standard H_2SO_4, is titrated with *N* NaOH. The difference in titre from a blank of the suspension gives the diacetate content plus the free acids. Two or three drops of alkali are added to the titration mixture, which is then extracted with ether. The aq. phase is acidified and steam-distilled to separate the acetic and benzoic acids and most of the cinnamic acid. The benzoic acid is determined by Mohler's method, and the cinnamic acid by titration with permanganate, in the presence and absence of acetate. The nitrobenzoic and nitrocinnamic acids, which are not steam-distilled, are extracted with ether and the nitrocinnamic acid is determined with permanganate. An aliquot of aldehydes in the ether phase (retained from the diacetate determination) is treated with hydroxylamine hydrochloride and the liberated acid is determined. Another aliquot is oxidised to acids which are determined as for the free acids. E. J. H. Birch

562. **The determination of chalkones.** W. Davey and J. R. Gwilt (The Polytechnic, Regent St., London). *Chem. & Ind.*, 1956, (35), 911–912.—The chalkone (≃ 0·2 g weighed accurately) is dissolved in 25 ml of aldehyde-free alcohol, and 75 ml of 2:4-dinitrophenylhydrazine soln. [1 g in 20 ml of 50% (v/v) H_2SO_4, with H_2O to 100 ml] is added slowly, with shaking. The mixture is heated under reflux in a boiling-water bath for 4 hr., cooled, diluted with 100 ml of 2% H_2SO_4, and left overnight. The pptd. derivative is filtered off, washed with H_2O until acid-free, and finally dried to constant weight at 80°. The identity of the chalkone may be confirmed by the melting point of the derivative; for complete characterisation, the derivative should be recrystallised from glacial acetic acid to constant melting point. Typical results are listed. O. M. Whitton

563. **Tetralin derivatives. IV. Reaction of hydroxytetralone oxime with various metal ions.** Tsutomu Momose and Yosuke Ohkura (Pharm. Inst., Medical Faculty, Kyushu Univ., Katakasu, Fukuoka). *Japan Analyst*, 1956, **5** (6), 332–335.—Several tetralone oximes were synthesised (Momose *et al.*, *Pharm. Bull. Japan*, 1954, **2**, 119; 1955, **3**, 441, in English) and it was found that those having an OH group in the 8-position yield inner complex salts with metal ions. Among them 8-hydroxy-5-methoxytetralone oxime was most useful in chemical analysis. It produces yellow ppt. with Cu in mineral or acetic acid soln. (limit of detection 5 μg) and pale-green ppt. with Ni in a neutral soln. (limit 1·5 μg). Both are sol. in chloroform and the soln. have max. absorption in the near-u.v. region. K. Saito

564. **X-ray powder diffraction patterns of benzoic acids.** H. A. Rose and A. J. Van Camp (Eli Lilly & Co., Indianapolis, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1430–1432.—X-ray diffraction data are given for the identification of 25 substituted benzoic acids. An example is given of the use of the X-ray pattern to differentiate between two compounds having the same empirical formula and melting point. G. P. Cook

565. **The separation and analysis of a mixture of benzoic, phthalic, trimesic and trimellitic acids.** G. Khodzhaev and A. P. Ibragimov. *Dokl. Akad. Nauk, UzSSR*, 1955, (8), 17–20; *Ref. Zhur., Khim.*, 1956, Abstr. No. 16,439.—Benzoic acid (**I**) is separated from the other acids with dried freshly distilled $CHCl_3$ and determined as described earlier (*Ibid.*, 1952, No. 10, 28). For the separation of terephthalic (**II**) and trimesic (**III**) acids from other aromatic acids, percolate dried freshly distilled acetone at 17° to 18° for ≃ 1 hr. through the mixture into a 150-ml flask. In the flask, phthalic (**IV**), *iso*phthalic (**V**) and trimellitic (**VI**) acids concentrate, while **II** and **III** remain in the funnel. To separate **V** from **IV** and **VI** in the acetone soln., distil off the acetone and dry the residue at 50°. Then add 100 to 120 ml of water and warm to between 50° and 60°. Cool the soln obtained to 2°; **V** is pptd., while **IV** and **VI** remain in soln. The quantity of **V** is determined as described earlier. Transfer the filtrate containing **IV** and **VI** in portions to a small beaker, evaporate to dryness, dry at 105° and weigh the mixed acids. The mixture is separated by Rodionov's method (*Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1937, 501). The dried residue containing **II** and **III** is extracted with H_2O at 60°. **III** dissolves. Transfer **II** from the funnel to a watch-glass, dry and weigh. Transfer the soln. of **III** to a porcelain basin, evaporate to a vol. of 25 to 30 ml, cool and add, with stirring, an excess of aq. NH_3, and then an excess of a 30% soln. of $BaCl_2$. Heat the basin until no more NH_3 can be smelt, cool, filter off the barium salt of **III**, wash with cold water 2 or 3 times, and dry at 120°. C. D. KOPKIN

566. **Polarographic behaviour of phthalic acid and some of its esters.** A. Ryvolová and V. Hanuš (Inst. Phys. Chem., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (1), 46–54.—In buffered solutions phthalic acid is reducible on the dropping-mercury electrode and yields three waves, its esters two, and some diesters only one wave. The height of the wave depends on the pH of the solution. The probable explanation of these waves is based on the assumption of various recombination possibilities, according to which phthalic acid in the first wave is reduced in the form of a cation, in the second wave as an undissociated molecule, and in the third as a univalent anion. The rate constants of dissociation and of recombination were calculated. Experiments dealing with the oscillopolarographic behaviour of phthalic acid were also carried out. J. ZÝKA

567. **Tetralin derivatives. III. Two cupferron analogues of tetralin.** Tsutomu Momose, Yu Ueda and Masatake Iwasaki (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *Japan Analyst*, 1956, **5** (5), 271–274.—Ammonium ar-α- and ar-β-nitrosohydroxylaminotetralin (**I** and **II**) were synthesised from α- and β-nitrotetralin and their use for the gravimetric and colorimetric determination of Fe and Cu was studied. Both **I** and **II** precipitate Fe from 10% HCl soln.; Cu, Al, Sn, Zn, Pb, Cd and Bi from 30% acetic acid; and Ag, Ni, Co, Mn, Cr, Ba, Sr, Ca, Mg and Hg from a neutral soln. (limit of detection, 0·3 μg per ml for **I**, 0·1 μg for **II**). Copper (> 5 μg) produces a grey ppt. with **I** or **II** in 30% acetic acid and can be gravimetrically determined; Fe can be similarly determined. The Fe complex is extractable with $CHCl_3$; the organic layer has a max. absorption at ≃ 400 mμ, its extinction coeff. being proportional to the amount of Fe for 10 to 100 μg per ml. The max. absorption of the Cu complex in $CHCl_3$ is at ≃ 600 mμ. K. SAITO

568. **Alkalimetric determination of salts of organic bases after precipitation in the form of tetraphenylboron salts. I. Long-chain quaternary ammonium salts.** J.-A. Gautier, J. Renault and F. Pellerin (Faculté de Pharm. de Paris). *Ann. Pharm. Franç.*, 1955, **13** (12), 725–730.—Several dimethylalkylbenzylammonium, trimethylalkylammonium, alkylpyridinium and alkyl*iso*quinolinium salts containing a long-chain alkyl group are determined. *Procedure*—The sample (0·25 milli-equiv.) is dissolved in 15 ml of water, and five drops of 10% aq. $AlCl_3$ are added to aid coagulation of the ppt.; after adjustment of the pH to between 4 and 5, Na tetraphenylboron solution is added in excess. After the mixture has been heated for 30 min. at 60° on a water bath, the ppt. is filtered off (porcelain G4) (in some cases after previous centrifugation) and washed with 1% acetic acid. The ppt. is dissolved in acetone, which is removed under reduced pressure, and the residue is dried at 60°. The residue is dissolved in 10 ml of anhyd. dioxan and titrated with 0·05 *N* $HClO_4$ in anhyd. acetic acid, with a drop of 1% methyl violet in acetic acid as indicator. For most of the compounds the error is < ± 1%. E. J. H. BIRCH

569. **Photometric estimation of some aromatic amines by means of the Lauth reaction.** J. Jan, J. Kolšek and M. Perpar (Inst. Org. Chem., Univ., Ljubljana, Jugoslavia). *Z. anal. Chem.*, 1956, **153** (1), 4–11.—In the photometric determination of aromatic amines by oxidation with PbO_2, the replacement of acetic acid by H_3PO_4 gives more stable colours. By this method, it is possible to determine monomethyl-, dimethyl- and diethylaniline, di- and tri-phenylamine, ethyldiphenylamine, *m*-toluidine and aniline in concn. from < 1 μg per ml to 10 μg per ml. *Procedure*—Water-soluble amines are dissolved in 3 *M* H_3PO_4, and sparingly sol. amines in 3 *M* H_3PO_4 in 50% ethanol. To a suitable aliquot, after dilution to 15 ml with the same solvent, is added 200 mg of PbO_2. After allowing the soln. to stand for 10 min., with occasional shaking, the excess of PbO_2 is removed by centrifuging, and the extinction of the soln. is measured within 10 min. in 1-cm cells. J. H. WATON

570. **Titration of drugs and chemicals in non-aqueous solutions. X. Effect of other acids on the titration of inorganic and organic bases in glacial acetic acid.** Tetsu Kashima and Koichiro Kano (National Hyg. Lab., Tamagawayoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (1), 50–53.—The effect of various acids on the titration of organic bases (*e.g.*, diphenylamine) with $HClO_4$ in glacial acetic acid was studied with HI, HBr, HCl, HNO_3, H_2SO_4, H_3PO_4, oxalic, picric and maleic acid; the magnitude of interference decreases in the order given. Other organic acids, including formic, lactic, citric, benzoic and salicylic, have no significant influence on the titration. The potentiometric titration curves are discussed on the basis of acidity function of these acids; their relative strength appears to be identical with that in an aq. soln. K. SAITO

571. **The determination of organic bases with hexanitrodiphenylamine. II. The determination of pyridine with special reference to the determination of pyridine in alcohol.** S. Kertes and V. Kertes

(Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **15** (2), 154–157.—The reaction between 2:4:6:2′:4′:6′-hexanitrodiphenylamine and pyridine to produce an orange or red colour (*cf. Anal. Abstr.*, 1956, **3**, 3679) has been investigated and the following methods of analysis have been evolved. *Detection of pyridine*—To 3 drops of the test soln. add 5 drops of a 0·1 *M* soln. of hexanitrodiphenylamine in dioxan. An orange colour is produced with $\lt 4$ μg of pyridine, or with 2 μg in a total vol. of 2 drops if the reaction is carried out on a spot plate. *Determination of pyridine*—To 8 ml of the reagent soln. add 2 ml of the test soln. and determine the extinction at 540 mμ. For 0·1 to 1 mg of pyridine the reagent soln. is 0·01 *M* in dioxan; for 1 to 10 mg a 0·01 *M* soln. is used; these soln. must be freshly prepared and the method must be calibrated for each batch of soln. Methanol, ethanol and acetone do not interfere under the specified conditions; water ($> 5\%$) interferes in the determination of low concn. of pyridine. Organic and inorganic bases must be absent. *Determination of pyridine in denatured alcohol*—To 5 ml of the 0·01 *M* reagent soln. in dioxan add 3 ml of dioxan and 2 ml of the ethanol containing $\simeq$ 5% of pyridine, and proceed as above. Methanol and water, both normally present in denatured alcohol to the extent of 2·5% and 5%, respectively, do not interfere. W. C. JOHNSON

572. **Conductimetric titrations of organic bases with boron tribromide in aprotic solvents.** M. C. Henry, J. F. Hazel and W. M. McNabb (Univ. Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1956, **15** (2), 187–192.—The reactions between various organic bases and BF_3 in non-aqueous solvents have been studied on the basis of conductimetric titrations. Conductimetric curves are reproduced for the titration of BF_3 with (*i*) pyridine and (*ii*) quinoline in nitrobenzene, of BF_3 with (*iii*) *iso*quinoline and (*iv*) quinoline in thiophosphoryl chloride, of BF_3 with (*v*) α-picoline and (*vi*) *iso*quinoline in thionyl chloride and of (*vii*) pyridine and (*viii*) 5-ethyl-2-methylpyridine with BF_3 in thionyl chloride. The course of each reaction is discussed in terms of the electronic theory. Analytical precision is attained in the end-points. W. C. JOHNSON

573. **Separation of pyridine bases by vapour-phase chromatography.** V. T. Brooks and G. A. Collins (Midland Tar Distillers Ltd., Four Ashes, Wolverhampton). *Chem. & Ind.*, 1956, (38), 1021.—The separation of some 16 pyridine bases, including the picolines, lutidines and collidines, by means of different stationary phases has been investigated. Many of these compounds may be satisfactorily separated on columns containing liquid paraffin, trixylyl phosphate, polyethylene glycol 1000 and silicone M.430, but β- and γ-picolines can be separated only by using either triethanolamine or glycerol. C. A. SLATER

574. **Fission of the pyridine ring as an analytical principle.** H. Freytag (Ondal, G.m.b.H., Hunfeld/Hessen, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 86–96.—Possible analytical applications of the fission of the pyridine ring are discussed and examined. Pyridine may be used in the form of a reagent paper and the ring split by u.v. irradiation. The product is useful for the detection of pyrrole (0·7 μg in 0·01 ml of methanol) [blue spot in the presence of HCl (1:1)], of *iso*thiocyanatoacetic acid (**I**) (234 μg in 0·02 ml) (brown - violet spot with 0·1 *N* HCl), and of rhodanine (**II**) (27 μg in 0·02 ml) [greenish spot with HCl (1:1)] and can be used to differentiate between **I**, **II** and pseudohydantoin. Alternatively, pyridine may be used as liquid and split by chemical means. Such reactions are used for the detection of sulphonated oils, of chlorinated acetic acid, and of nicotinamide in the presence of trichloroacetic acid. The sensitivity of the test for trichloroacetic acid is particularly high (0·02 μg in 0·1 ml). Quaternary salts of pyridine are detected by heating with 30% NaOH soln. and condensing the product with 2-naphthylamine; on addition of HCl a red colour develops. J. P. STERN

575. **Determination of small amounts of γ-picoline in aqueous solutions of β-picoline by vapour-phase chromatography.** W. J. Murray and A. F. Williams (I.C.I. Ltd., Nobel Div., Stevenston). *Chem. & Ind.*, 1956, (38), 1020–1021.—A method for the separation of α-, β-, and γ-picolines and 2:6-lutidine on a column of glycerol - Celite 535 (30:100) at 78° is described. With a column 4 ft. long and 4 mm in diameter and with nitrogen gas it is possible to estimate less than 0·2% of γ-picoline in β-picoline in aqueous soln. containing 75% of water. C. A. SLATER

576. **Determination of pyrazinamide. I. Colour reaction and colorimetric determination of pyrazinamide.** Kiichiro Kakemi, Toyozo Uno and Hitoshi Seno (Pharm. Inst., Medical Faculty, Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (3), 273–275.—It was found that pyrazinamide (**I**) reacts with sodium nitroprusside (**II**) in Na_2CO_3 soln. to give an orange - red colour having max. absorption at 494 mμ, and its use for the colorimetric determination of **I** is suggested. The hydrolysis product, pyrazinoic acid (**III**), undergoes a similar reaction showing max. absorption at 470 mμ, but is removed with an anion-exchange resin. The sample soln. (1 to 30 μg per ml, 5 ml) is treated with 0·1% **II** soln. (1 ml) and 10% Na_2CO_3 (a few drops) in a water bath (40°) for 5 min., and the extinction is measured at 494 mμ. The working curve is linear for $\lt 30$ μg of **I** per ml. In the presence of **III**, the sample soln. is passed through a column (diameter 7 mm, length 30 mm) of Diaion A or Amberlite IRA-400 and **I** is similarly determined in the eluate with 0·6% **II** soln. (1 ml) and 20% Na_2CO_3 (2 ml). **I** also reacts with Na pentaamminocyanoferrate (0·1% aq. soln.) (red coloration) in a neutral soln. and with a soln. of *p*-dimethylaminobenzaldehyde in conc. H_2SO_4 (yellow coloration); both tests are used for the identification of **I** (limit of detection 1 μg per ml for the former and 10 μg for the latter). K. SAITO

577. **Separation of gases by gas-adsorption chromatography.** S. A. Greene, M. L. Moberg and E. M. Wilson (Aerojet-General Corp., Azusa, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1369–1370.—The separation and quant. analysis of some low-boiling gases and hydrocarbons by gas chromatography, on activated charcoal or alumina-packed columns, is described. During elution the column temp. is continually increased. The procedure is advantageous for analysis of mixtures with wide boiling ranges, as it sharpens peaks, improves peak symmetry and reduces the analysis time. The precision of the determination of four hydrocarbons was within $\pm$ 2·0%. G. P. COOK

578. **Gas - liquid chromatography. Separation of hydrocarbons using various stationary phases.** V. T. Brooks and G. A. Collins (Res. Dept., Midland Tar

Distillers Ltd., Four Ashes, Wolverhampton, England). *Chem. & Ind.*, 1956, (35), 921.—By a suitable selection of the fixed phase, a gas - liquid chromatography column may operate either as a highly efficient thermal distillation column or as a chromatographic column, separating according to molecular types. When a non-polar material such as liquid paraffin is used there is little separation of different types of hydrocarbon boiling at about the same temp., but very good separation within a homologous series. As the polarity of the phase is increased, aromatics are held back on the column relative to aliphatics, and with a poly(ethylene glycol) the aliphatic hydrocarbons boiling below about 200° are almost completely separated from aromatics boiling in the same range. The separation of homologues is not as good as when a non-polar phase is used. Some results are presented.
O. M. WHITTON

579. **Analytical separation and identification of sulphur compounds in a petroleum distillate boiling to 100°C.** H. J. Coleman, N. G. Adams, B. H. Eccleston, R. L. Hopkins, L. Mikkelsen, H. T. Rall, D. Richardson, C. J. Thompson and H. M. Smith (Bureau of Mines, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1380–1384.—The sulphur compounds present in a crude oil in the boiling range 0° to 100° were identified and determined. The separation processes used were isothermal distillation, fractionation, concentration by adsorption on alumina and semi-micro fractionation of the concentrate. Identification and determination were achieved by i.r. analysis. Fifteen sulphur compounds were found in a Texas crude oil and are listed. G. P. COOK

580. **Gas partition analysis of light ends in gasolines.** D. H. Lichtenfels, S. A. Fleck, F. H. Burow and N. D. Coggeshall (Gulf Res. and Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1956 **28** (9), 1376–1379.—A gas - liquid partition chromatographic method is presented for the rapid separation, identification and determination of light components in petrol and similar products. The apparatus consists of two columns in series, the first being a short column to strip the light fraction from heavier components and the second column to provide a more complete analysis of the lighter fraction. Analysis of C_5 and lighter components in a cracked petrol sample gave results in close agreement with a method involving distillation plus mass spectrometry. Analysis of a synthetic sample gave recoveries $> 95\%$. G. P. COOK

581. **Rapid determination of petrol vapour with a detector tube.** Yoshitaka Kobayashi (Faculty of Eng., Yokohama Univ., Mimami-ku, Yokohama). *Japan Analyst*, 1956, **5** (7), 409–410.—A sensitive detector tube (Kobayashi *et al.*, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1953, **5** , 809) was used for the estimation of petrol vapour in the atmosphere (limit of detection, 0·03 μg for *n*-hexane). Chromic acid (10 g) and H_2SO_4 (25 ml) are dissolved in water to a vol. of 100 ml and mixed with silica gel (40 to 60 mesh, 100 g); the product is dried below 100° to give a water content of $< 5\%$. The dry material (0·2 g) is packed in a thin-glass tube (diameter 2 mm, length of the gel column 60 to 80 mm). The sample air is passed through the tube (30 ml in 150 sec.) and the length of dark-green layer is measured; the amount of petrol is calculated from an empirical table. The working curve is linear for 10 to 80 mg per ml, irrespective of the sort of hydrocarbon. Methane and ethane are inactive to this detector. Interference results from most organic compounds. K. SAITO

582. **Paper chromatography of a petroleum porphyrin aggregate.** H. N. Dunning and J. K. Carlton (U.S. Dept. of the Interior, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1362–1366.—Paper-strip and paper-sheet chromatographic methods are described for the separation of the porphyrin aggregate of crude oil into several groups. A mixture of light petroleum and 2:4-lutidine is used as solvent and the porphyrin groups are characterised by their R_F values relative to that of aetioporphyrin II and by their absorption spectra. Seven groups were obtained from a Californian oil, the first two being characterised by spectra of the aetio type; the remaining groups gave phyllo-type spectra. G. P. COOK

583. **The separation and identification of some volatile paraffinic, naphthenic, olefinic and aromatic hydrocarbons.** A. T. James and A. J. P. Martin (Nat. Inst. for Med. Research, Mill Hill, London). *J. Appl. Chem.*, 1956, **6** (3), 105–115.—A gas-chromatographic apparatus in which several stationary phases adsorbed on kieselguhr are used, is described, and the relative retention volumes with nitrogen as the mobile phase are measured at 65°, 78·6° and 197° for a number of hydrocarbons. The apparatus has an efficiency of 1000 to 2000 theoretical plates for a 4-ft. length. The relationships between log retention volumes for the hydrocarbons on various stationary phases is discussed and methods of separation and identification are deduced. E. J. H. BIRCH

584. **The determination of naphthalene in gas. A comparison of the picrate and ultra-violet methods.** A. B. Densham and E. M. Seaton (Fulham Research Lab., Gas Works, Kings Road, London). *J. Appl. Chem.*, 1956, **6** (3), 101–105.—The picrate method of Ravald and Chilver for the determination of naphthalene in coal gas is published for the first time. The gas drawn from the main passes through a trap containing 10% H_2SO_4 for pyridine and ammonia and then through absorption bottles containing 100 ml of $N/30$ or $N/22$ aq. picric acid, depending on the temp. Any solid naphthalene condensing in the tubes is washed in with a little acetone. The solid picrate is filtered off, washed, and taken up in neutral $CHCl_3$. Half the $CHCl_3$ solution is titrated with 0·1 N NaOH, with lacmoid as indicator. Any unsaturated compounds forming picrates are corrected for by determining with Wijs solution in the other half of the solution. The u.-v. method enables naphthalene and 1- and 2-methylnaphthalene to be determined separately. The naphthalenes are absorbed in specially purified Carless petroleum distillate (boiling range 210° to 250°) and the extinctions are measured at 311, 314 and 319 mμ, the absorption maxima for the three naphthalenes. The concn. of the three substances in terms of the three extinctions are given. Comparison of the results shows that the picrate method gives a result concordant with the total of naphthalene and methylnaphthalenes. E. J. H. BIRCH

585. **Identification of thiophen and 2-methylthiophen in virgin petroleum.** C. J. Thompson, H. J. Coleman, L. Mikkelsen, D. Yee, C. C. Ward and H. T. Rall (Bureau of Mines, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1384–1387.—A Californian crude oil was analysed to determine whether thiophen as such exists in virgin petroleum or whether it is produced by pyrolytic

breakdown or rearrangement of other sulphur compounds. The crude oil was exposed to a maximum temp. of 100° for less than 30 sec. in the preparation of the distillate from which thiophen was concentrated. Confirmation of the presence of thiophen and 2-methylthiophen was obtained by mass spectrometry, i.r. absorption, and with the isatin and alloxan colour tests. The 2-methylthiophen and thiophen contents of the oil analysed are estimated to be not less than 0·0001% and 0·000032%, respectively. G. P. Cook

586. **Determination of asphalt in brown-coal tars and hydrogenation products.** R. Tannenberger (VEB Kombinat 'Otto Grotewohl', Böhlen, Leipzig, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 193–203.—Asphalt is pptd. from brown-coal tar by lubricating oil at 50°. The ppt. is voluminous and powdery; formation of gummy material is avoided by keeping the temp. below the m.p. of the asphalt. Addition of *n*-hexane then completes pptn. and provides a filterable asphalt. Reproducibility is within ± 5% of the asphalt content, which lies between 3 and 12% for tars of different origin. J. P. Stern

587. **The determination of the tar content of distillation coke and lignite briquettes.** R. Herrmann and F. Obendorf. *Chem. Tech., Berlin*, 1956, **8** (6), 331–333.—A new and rapid distillation method, with all-glass apparatus, is described and compared with the standard Fischer method, in which an aluminium retort is used, and with production results. The rate of heating is carefully controlled and heating curves are given. The results for the quantity of volatile tars by all three methods are in good agreement, both for coke and lignite. Results of the determination of residual coke, and carbon and hydrogen analysis of the distillation products of the new method are in better agreement with production results than the results obtained by the Fischer method. The new method takes only 12 min. for coke and 24 min. for coal and is more economical. P. S. Stross

588. **Titration in non-aqueous medium. I. Determination of pyridine bases in tar products.** J. Minczewski and Z. Łada (Inst. Gen. Chem., Warsaw). *Roczn. Chem.*, 1955, **29**, 948–949.—Pyridine bases in tar middle oil were determined in the presence of NH_3 and acidic constituents by dissolving the sample in a mixture of glacial acetic acid and formaldehyde and titrating potentiometrically with 0·1 *N* $HClO_4$ in acetic acid. A silver - silver chloride electrode dipped in a saturated soln. of KCl in acetic acid, and a glass electrode, were used. Two inflection points were observed, the first for NH_3 and the second for the total of the pyridine bases.

II. Determination of phenols in tar products. J. Minczewski and Z. Łada. *Ibid.*, 1955, **29**, 950.—Phenolic constituents in tar distillation products containing NH_3 and pyridine bases were determined by dissolving the sample in anhyd. pyridine or aniline and titrating potentiometrically with 0·1 *N* K methoxide in a mixture of methanol and benzene (1:6). A silver - silver chloride electrode dipped in a 10% soln. of LiCl in methanol and an antimony electrode were used. Chem. Abstr.

589. **Determination of micro amounts of mineral oils in organic solvents and on metal parts.** B. D. Luft and E. S. Sher. *Zavod. Lab.*, 1956, **22** (7), 784–787.—Two methods are described. For semi-quant. work, 5 or 6 drops of the oil-containing soln. are placed on a marked spot on a filter-paper which has been first treated with a 1% soln. of dimethylglyoxime in ethanol, then air-dried, immersed in an ammoniacal soln. of $Ni(NO_3)_2$, washed with water and with ethanol and again dried. After evaporation of the solvent, the residue of oil is immersed in 15% H_2SO_4 soln. The paper becomes decolorised except where it is protected by the oil. Under standard conditions the colour of the protected spot is a measure of the amount of oil present over the range 0·01 to 3 g per litre. The colour is compared with a series of standards. Quantitatively, the soln. of the oil in trichloroethylene, $CHCl_3$ or dichloroethane is examined photometrically at 250 to 400 mμ, and extinctions at suitable wavelengths are measured. A knowledge of the type of oil is necessary for the purpose of preparing standards. G. S. Smith

590. **Use of ASTM slope for predicting viscosities [of lubricating oils].** E. E. Klaus and M. R. Fenske (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Bull. A.S.T.M.*, 1956, No. 215, 87–94.—The ASTM slope method for expressing viscosity - temp. characteristics of lubricants is discussed; it is valid over a wider range than the viscosity - index method, which becomes inaccurate at index values > 150. Procedures are given for measuring the kinematic viscosities of mineral oils, esters and polymer-containing oils between 700° and −65° F. The combined use of three or four measured viscosities and the ASTM slope for the max. operating temp. interval, *e.g.*, −40° to 100° F or 350° to 700° F, should express adequately the viscosity - temp. characteristics of most machine oils and lubricants. The viscosities should preferably be measured at the extremes of the temp. range encountered in practice. W. J. Baker

591. **Application of paper chromatography to the analysis of dyes.** F. Kacprzak and Z. Olszewski (Inst. Barwników i Półproduktów, Łódź, Poland). *Przem. Chem.*, 1955, **11**, 677–679.—The value of paper chromatography in the analysis of dyes is discussed. Suitable types of filter-paper are recommended. Several techniques are recommended, including descending, ascending, two-dimensional and paper-disc chromatography. Cellulose powder was found to be useful in the form of columns similar to those employed for adsorption chromatography. The R_F values are similar to those obtained on filter-paper. All types of dyes can be tested by these techniques. The authors recommend the following solvents for general use—ethanol - water (80:20), ethanediol - water (60:40), methanol - water (60:20), *iso*butyric acid - water (80:20), and *iso*butyl alcohol - acetic acid (400:75). Solvents recommended for particular types of dyes are, for acidic dyes, dyes containing chromium and metal complexes—80% ethanol, 80% methanol, 60% ethanediol and 80% *iso*butyric acid; for basic dyes—80% ethanol and 80% methanol; for direct dyes—pyridine - methanol - water (60:35:5), pyridine - ethanol - water (60:35:5) and pyridine - 80% ethanol (60:40). K. F. Sporek

592. **Qualitative identification of synthetic fibres.** S. Schwenkedel. *Textil-Praxis*, 1955, **10**, 918–920.—Concentrated H_2SO_4, 5% NaOH, glacial acetic acid, acetone, benzene, *m*-cresol, alkaline Pb acetate, formic acid and methylene chloride are used either at room temp. or hot to identify and differentiate poly(vinyl chloride) compounds (Pe–Ce,

Vinyon), polyamides (Perlon L, Perlon T), polyurethanes (Perlon U), polyesters (Terylene, Dacron), and polyacrylonitriles (PAN, Orlon). Dye-staining with Neocarmine W (together with the so-called J. G.-modification staining) serves to differentiate these fibres. By dry distillation, the acidity or alkalinity of the vapours permits some measure of fibre origin. The burn test gives only a very rough estimation of fibre identity, but comparison burn-tests with known fibres are indispensable. To separate fibres, immerse the sample in CCl_4, which will dissolve poly(vinyl chloride) and leave the other four fibre categories undissolved; apply hot formic acid, which dissolves the polyamides and polyurethanes, leaving the other fibres undissolved; and finally dissolve the polyester fibres in *m*-cresol, leaving the polyacrylonitriles undissolved. Several special fibre reactions are useful for confirmation. Poly(vinyl chloride) can be identified by the Beilstein test along with the very low softening-point of these fibres. Polyacrylonitriles can be recognised readily by the intense red-brown coloration produced on boiling with 10% NaOH (saponification of nitrile groups), while the escaping vapours give a positive test for NH_3. Perlon L and nylon can be differentiated by 50% formic acid at 80°, which dissolves Perlon L and causes nylon to crumple together; by 80% acetic acid at boiling point, which dissolves Perlon L and causes nylon to crumple and eventually dissolve; by 4·2 *N* HCl at room temp., which dissolves Perlon L while nylon dissolves only at boiling point. Melting-point determination is by means of the melting-point salt (Merck) (m.p. 220°); Perlon melts at 215°, while nylon (m.p. 250°) remains intact.

CHEM. ABSTR.

593. **Analysis of viscose solutions.** B. Philipp (Lab. for Org. Syntheses, Leipzig, Germany). *Chem. Tech., Berlin*, 1956, **8** (2), 77–81.—A discussion is given of the relative accuracy and suitability for works control and for accurate work of methods of analysis of viscose. The methods are those for determining total S (**I**), xanthate (**II**) and COS (**III**); potentiometric methods for the stage-wise estimation of sulphide S, thiocarbonate and xanthate are also discussed. The usual works method for estimating **I** (oxidation to sulphate with H_2O_2 in alkaline soln. and titration of the loss of alkali) is the one best suited to works control; the results are about 16% too high and a correcting factor must be used. Of the alternative methods for estimating **I**, the gravimetric method (as $BaSO_4$ after bromine oxidation) gives the most dependable results, but the method comprising decomposition of the viscose with dil. acid and estimating the resulting H_2S and CS_2 iodimetrically is more rapid, and gives results of similar accuracy. For works control estimation of **II**, the iodimetric method of Geiger (*Helv. Chim. Acta*, 1930, **3**, 281) is recommended for its speed, but the results should be checked by the longer and more accurate method of pptg. the viscose with diethylchloroacetamide or chloroacetonitrile and making a Kjeldahl determination of the resulting ppt.; alternative methods of estimating **II** are discussed. A method is devised for estimating **III** by selective absorption of the COS with ammoniacal $CaCl_2$ soln.; (*Faserforsch. u. Textiltech.*, 1955, **6**, 13); any CS_2 present does not react and < 0·2 mg of COS can be determined. The potentiometric estimation of sulphide S, thiocarbonate and xanthate (by pptn. with $AgNO_3$) is also discussed.

H. L. WHITEHEAD

594. **The determination of formaldehyde in paper for photographic-paper manufacture.** W. Taube (Kodak, A.-G., Berlin). *Chem. Tech., Berlin*, 1956, **8** (6), 333–336.—The determination of formaldehyde in paper intended for photographic use is necessary because formaldehyde interferes in the photochemical processes. The chromotropic acid method was found to be more satisfactory than the phloroglucinol method and gives results in agreement with the titrimetric hydroxylamine hydrochloride method. Clear aq. paper-extracts can be estimated directly; hazy extracts must be distilled in an apparatus designed to avoid bumping and frothing. Acid should not be used for the extraction as high results are obtained. Mix 2 ml of extract or distillate (representing 2 sq. cm of paper) with water (3 ml) and freshly prepared chromotropic acid solution (to 100 ml of conc. H_2SO_4 add 2 ml of 5% aq. chromotropic acid soln.) (5 ml). Set aside for 10 min.; dilute with water (10 ml), measure the extinction after a further 10 to 20 min. and calculate the formaldehyde from a calibration curve.

P. S. STROSS

595. **Polarographic determination of citral in plants.** J. Holubek (ForschInst. Heilpflanzen, Prague, Czechoslovakia). *Pharm. Zentralh.*, 1956, **95** (4), 129–134.—A simple polarographic method for the determination of citral in the essential oils derived from the plants is described and results are compared with those from other methods. Transfer 0·03 to 0·04 ml of the essential oil, distilled from the plant, and dilute with ether in a 50-ml flask. Evaporate off most of the ether and make up to 50 ml with 0·1 *N* LiCl in alcohol [60% (v/v)]. To 5 ml of this soln. in a polarographic cell add 5 drops of gelatin solution (0·5%), pass a stream of N and polarograph. The wave height is proportional to the citral concentration.

P. S. STROSS

596. **Chromatographic determination of hydrocarbons in rose oil.** D. Ivanoff, N. Marécoff, St. Pavlova and L. Ivanova (Univ. of Sofia, Bulgaria). *Ind. Parfum.*, 1956, **11**, 105–106.—Established methods of assay for Bulgarian rose oil determine total hydrocarbons as 'stearoptene'. This contains all matter that is insoluble in ethanol (75%) and is solid at 0° and includes aromatic bodies. The method described separates only the hydrocarbons. *Procedure*—Prepare a chromatographic column of Al_2O_3 (≃ 120 g) (2 cm in diam. × 40 cm). Accurately weigh a sample of the oil (2 g) and dissolve it in light petroleum (boiling range 30° to 50°). Transfer the soln. to the column and collect one fraction of 30 ml and then fractions of 20 ml. Remove the solvent at 60° until the residue is of constant weight. The results show a loss of ≃ 1·5% of total hydrocarbons on mixtures of known composition.

H. B. HEATH

597. **Colorimetric determination of phenolic resins.** M. H. Swann and D. J. Weil (Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1463–1465.—The procedure is based on the nitrous acid test for phenols. An intense yellow colour is produced when this test is applied to phenolic resins dissolved in a water-insol. solvent such as butyl acetate or *n*-hexanol. It is specific for phenolic resins and gives highly reproducible results. Recoveries for varnishes, made from drying oils and *p*-phenylphenol-formaldehyde resins, were > ≃ 70%.

G. P. COOK

598. **Field kit for estimating moisture in acrylic moulding powder by a small sealed vessel technique.** C. F. Roth and J. Mitchell, jun. (E. I. du Pont de Nemours and Co. Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1502–1504.—The field kit described is suitable for use with a method based on the titration of a $CHCl_3$ soln. of the polymer with standardised Karl Fischer reagent. An accuracy within ± 10% relative in the range 0 to 0·5% of moisture can be attained.

G. P. COOK

599. **Rapid determination of chlorine content of rubber hydrochloride by means of density gradients in centrifugal field.** G. Schuur and A. Klootwijk (Rubber-Stichting, Delft, Holland). *Anal. Chem.*, 1956, **28** (9), 1455–1457.—The use of centrifugation in a liquid of graduated density for the determination of the density of suspended particles is described and applied to rubber hydrochloride prepared from latex. The method is applicable to both chlorinated and cyclised rubbers with little alteration. The density gradient consists of three layers partially mixed at the interfaces, each containing 1% of Emulphor O (a non-ionic detergent) and a trace of HCl, the lowest layer consisting of 22% NaCl soln. with bromothymol blue, the middle layer 16% NaCl and the upper layer 10% NaCl with methyl red; these are contained in a tube (190 mm × 10 mm). Calibration of this gradient with a non-volatile oil mixture enables the density of rubber hydrochloride in the range 24 to 33% Cl to be determined in 10 min. per sample. Differences of 0·1% in chlorine content are detectable.

E. G. CUMMINS

600. **Correlation of tannin content with tannin - formaldehyde precipitate.** F. R. Humphreys (Div. Wood Technol., 96 Harrington St., Sydney, Australia). *J. Soc. Leath. Tr. Chem.*, 1956, **40** (5), 147–149.—A rapid method was required for determining the tannin content in barks that are a potential source of tannin. The tannin content of *Pinus radiata* bark has been shown to be a linear function of the tannin - formaldehyde percentage. Details are given for the extraction of tannin from bark and pptn. with formaldehyde; the tannin - formaldehyde ppt. obtained is heated to constant wt. and weighed, and the value corrected for the moisture content of the original sample. Tannin content % = $0{\cdot}76x - 3{\cdot}45$ (where x = % tannin - formaldehyde ppt.).

B. R. HAZEL

601. **Official methods of leather testing recommended by the committee for physical testing of leather.** Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1956, **40** (5), 150–162.—Recommended amendments are given for the S.L.T.C. Official Methods for measurement of apparent density, water absorption, surface shrinkage, resistance to compression, buckle-tear, indentation index, resistance to grain crack, and water penetration pressure.

B. R. HAZEL

602. **Official methods of leather testing recommended by the committee for the chemical analysis of chrome tanned leathers and chrome tanning materials.** Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1956, **40** (5), 163–169.—Details are given of the Official Methods of Analysis of the S.L.T.C. incorporating amendments recommended by the Committee. Methods given are for the determination of chromium in leather, analysis of liquid or solid fresh chrome tanning materials, and for the determination of acid combined with chromium in chrome tanning materials, Cr in used liquors, and the pH of the liquors.

B. R. HAZEL

603. **Radioassay of tagged sulphate impurity in cellulose nitrate.** S. Helf, T. C. Castorina, C. G. White and R. J. Graybush (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1465–1468.—Two different radioassay methods of determining the sulphate impurity (≃ 0·005%) in cellulose nitrate are described. The H_2SO_4 used in the nitrating mixture is labelled with ^{35}S, and the cellulose nitrate is assayed for radioactivity, either from a layer of infinite thickness of fixed area, with a windowless gas counter, or when dissolved in a liquid phosphor solution (2:5-diphenyloxazole in toluene) with a liquid scintillation counter.

E. G. CUMMINS

See also Abstracts 355, 769.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

604. **Complexiметric titration of potassium in blood serum.** H. Flaschka and A. Holasek (Med.-Chem. Inst. und Pregl Lab. der Univ. Graz, Austria). *Hoppe-Seyl. Z.*, 1956, **303** (1–2), 9–13.—The treatment of the serum and the pptn. are as in the classical cobaltinitrite methods (Kramer and Tisdall, *J. Biol. Chem.*, 1921, **46**, 339), but instead of oxidimetric titration of the nitrite in the ppt., complexiметric titration of the cobalt is substituted. Errors due to oxidation of co-pptd. organic particles are thereby avoided. *Procedure*—To the serum (1 ml) in a 10-ml centrifuge tube add 2 ml of the cobaltinitrite reagent. Mix and set aside for 45 min. Then centrifuge and wash three times with cold double-distilled water. Shake the ppt. with conc. HCl (1 ml), add a few crystals of urea and place in a boiling-water bath. When solution is complete, and the originally brown liquid is colourless, add conc. aq. NH_3 (2 ml) and a sufficient quantity of NaCl and murexide (200:1, w/w) to make the mixture deep yellow. Titrate with 0·001 *M* EDTA, proceeding very slowly after the liquid has turned red. The end-point is reached when further addition of EDTA produces no deepening of the final violet colour.

F. POWELL

605. **A sensitive, accurate spectrophotometric method for the determination of magnesium in serum.** R. M. Levine and J. R. Cummings (Dept. of Pharmacol., Tufts Univ. Sch. of Med., Boston, Mass., U.S.A.). *J. Biol. Chem.*, 1956, **221** (2), 735–742.—A method is described for the determination of 5 μg of Mg per ml of serum or plasma with Eriochrome black T as the reagent. The Ca is first pptd. as Ca oxalate from 1 ml of serum, and after pptn. of protein with trichloroacetic acid the Mg is determined in the supernatant liquid by reaction with the dyestuff in the presence of a piperidine buffer and ethanol. The extinction of the resulting coloured solution is measured spectrophotometrically at 520 mμ. A reagent control is carried out at the same time to eliminate the interference due to the added oxalate.

J. N. ASHLEY

606. **Enzyme tests for the detection of glucose.** J. A. Hunt, C. H. Gray and D. E. Thorogood (King's College Hospital, London). *Brit. Med. J.*, 1956, 586–588.—Two tests developed commercially for detecting glucose in urine have been critically investigated. In both methods, test papers consisting essentially of filter-paper impregnated with glucose oxidase, *o*-tolidine, and a vegetable peroxidase are dipped into the urine and then withdrawn. Any glucose present is oxidised by atmospheric O in the presence of oxidase to gluconic acid and H_2O_2, and the H_2O_2 reacts with the *o*-tolidine to produce a blue pigment. In one method the papers are also impregnated with a yellow dye so that colour changes from light green to dark blue are given with increasing concn. of glucose. Both tests are highly specific for glucose and are of potential value in supplementing existing qual. tests, but for quant. work they are not reliable and are of little value in the control of diabetes.

H. F. W. KIRKPATRICK

607. **Micro-determination of blood glucose by non-reductive method.** R. S. Martin (Hosp. for Mental Diseases, Brandon, Manitoba, Canada). *Chemist Analyst*, 1956, **45** (3), 73–75.—*Procedure*—Whole or citrated blood (0·05 ml) is added to an isotonic soln. (1·85 ml; 9·6 g of $Na_2SO_4.10H_2O$ and 2·1 g of $CuSO_4.5H_2O$ in 350 ml of H_2O) in a conical centrifuge tube. Sodium tungstate soln. [0·1 ml; 10% (w/v)] is added and the soln. is agitated. The ppt. is removed by centrifugation and the supernatant liquor (1 ml) is added to a test-tube, followed by conc. H_2SO_4 (3 ml), with cooling. The tube is immersed in boiling water for 7 min., cooled, and a soln. of phloroglucinol [1 ml; 0·4% (w/v)] is added. The soln. is heated at 37° for 7 min. and the intensity of the colour is measured immediately at 450 mμ. The amount of glucose is determined by reference to a standard curve. Results are in good agreement with those of other methods.

C. A. SLATER

608. **A simple colorimetric method for determining blood glucose.** N. Wahba, S. Hanna and M. M. El-Sadr (Ein Shams Univ., Cairo, Egypt). *Analyst*, 1956, **81**, 430–432.—The method described for the determination of blood glucose depends on the formation of a soln. of the yellow glucosazone, the intensity of the colour being proportional to the concn. of glucose. The blood sample is deproteinised by heating with zinc acetate soln. and filtering. An aliquot portion of the filtrate is treated in a test-tube with a phenylhydrazine hydrochloride reagent and acetic acid, and the test-tube is placed in a boiling-water bath for 1 hr., together with a blank tube and three standard tubes containing 0·5, 1·0 and 2 mg of glucose, respectively. After cooling and suitable dilution, the extinctions of the yellow liquids are measured in a Spekker absorptiometer, with an Ilford No. 601 violet filter. The reaction is apparently specific for ketoses and aldoses and ascorbic acid. The concn. of the last in blood is very low. Other non-carbohydrate constituents of de-proteinised blood do not interfere, neither do ammonium oxalate or sodium fluoride added to blood as anti-coagulants.

A. O. JONES

609. **A micro method for the determination of nitrogen.** T. Breyhan (Chem. Untersuchungslab., Forschungsanstalt für Landwirtschaft, Braunschweig-Völkenrode, Germany). *Z. anal. Chem.*, 1956, **152** (6), 412–417.—To determine ammonia-, amino- and amido-N in small amounts of dried organic matter, heat the sample (< 50 mg) with a mixture of NaOH (0·7 g) and sodium acetate trihydrate (0·1 g) in an iron crucible in a Jena-glass flask in a stream of N, and collect and titrate the NH_3 in the usual manner. Recovery is usually > 90%.

A. R. ROGERS

610. **Determination of arsenic in a sample of bone by radio-activation.** R. Michon. *Ann. Falsif.*, 1956, **49**, 284–288.—With the procedure described, concn. of As of the order of 10^{-8} g can be determined, in samples of human viscera or bone, with a max. error of $\simeq$ 5%; for concn. of $\simeq 10^{-9}$ g the error is $\simeq$ 10%. The washed sample, and $\simeq$ 10 mg of As_2O_3 as a blank, are irradiated in a nuclear pile. The activated sample is then dissolved in a mixture of H_2SO_4 and HNO_3 to which is added $\simeq$ 20 mg of inactive As as carrier during the subsequent separation of the whole of the As by distillation from conc. HCl in the presence of Cu_2Cl_2 (or $SnCl_2$), followed by pptn. of As with sodium hypophosphite at 90° to 95°. The content of As and the activity of the washed and dried ppt. are determined, and the amount of activated As is calculated by reference to measurements on the blank. The pptd. As should be free from other radioactive impurities; if it is not, a further dissolution, distillation and pptn. should be made. Germanium, Sb, Se, Te and Br should be absent. The half-life of ^{76}As is 26·8 hr.

W. J. BAKER

611. **The determination of manganese in biological material by activation analysis, with a note on the gamma spectrum of blood.** H. J. M. Bowen (A.E.R.E., Harwell, Berks.). *J. Nuclear Energy*, 1956, **3** (1–2), 18–24.—Traces of Mn in blood (0·024 μg in 0·1 ml) and other biological materials are determined as 2·5-hr. ^{56}Mn following pile irradiation of 0·1-ml aliquots in polyethylene, together with 5-μg Mn standards, for 2·5 hr. at 10^{12} neutrons cm^{-2} sec^{-1}. Carriers are added and the Mn is purified by pptn. as MnO_2, $MnCO_3$ (twice) and MnO_2; the final ppt. is washed, dried, weighed (for chemical yield) and beta-counted under an end-window Geiger counter. Eight irradiated samples can be treated in 2·5 hr., with chemical yields of 60 to 90%, and decontamination factors from Na and P of 2×10^8 and 400, respectively. The normal concentrations of Fe in blood are sufficient to cause a positive error of 20% in the results for Mn, owing to the reaction—^{56}Fe (n,p) ^{56}Mn, from fast neutrons. An attempt at direct estimation of ^{56}Mn in irradiated whole blood by gamma spectrometry failed owing to swamping of the ^{56}Mn gamma emissions at 0·82 and 1·77 MeV by gammas from the activation products of Na and of Cl.

E. N. JENKINS

612. **The quantitative determination of Kollidone [poly(vinylpyrrolidone)].** R. Ammon and W. Nübling (Physiol.-Chem. Inst. Univ. Saarland, Hamburg, Saar). *Arzneimittel-Forsch.*, 1956, **6** (9), 565–567.—The Zipf method (*Klin. Wochschr.*, 1944, **23**, 340) for the determination of poly(vinylpyrrolidones) is studied and modifications are applied for estimating these substances in blood and urine. It was shown that the rate of pptn. of poly(vinylpyrrolidones) of differing chain length is dependent on the concn. of trichloroacetic acid, and for each there is an optimum end concn. Modifications of the method are given for (*a*) urine—pretreatment with alcohol, and (*b*) blood—deproteinisation with uranyl acetate.

D. P. FELIX

613. **Determination of volatile C_1–C_8 aliphatic acids in biological liquids by paper chromatography.** J. Guillaume and R. Osteux. *Compt. Rend.*, 1955, **241**, 501–502.—The sample, estimated to contain $\simeq$ 0·01 mole of mixed volatile acids, is steam-distilled into an excess of NaOH; the distillate is concentrated to $\simeq$ 1 ml and Na is removed by addition of a calculated amount of Permutit 50. The resulting pure solution of the acids (5 to 10 ml) is neutralised with *N* morpholine solution, with cresol red indicator. The solution is then chromatographed on Whatman No. 3 filter-paper (57 cm × 46 cm) and developed by spraying with *o*-cresolphthalein (0·2 g per 100 ml) buffered with barbitone sodium. The acids form yellow spots on a garnet-coloured background. Of a large no. of solvents tested, only allyl alcohol and propane-1:2-diol gave satisfactory separation of formic and acetic acids. Three solvent mixtures are specified and R_F values for the various acids are tabulated. A method of separating *n*- and *iso*-acids is also briefly indicated.
S.C.I. Abstr.

614. **Detection of iodine-containing substances on paper chromatograms.** L. Dragúnová and P. Langer (Slovak Acad. Sci., Bratislava, Czechoslovakia). *Nature*, 1956, **178**, 537–538.—By adding ferroin to the ceric sulphate - arsenous acid reagent (*Anal. Abstr.*, 1955, **2**, 735) (final concn. 0·01 to 0·0066 *M*), red spots on a blue background are obtained. The colour is stable for $\simeq$ 48 hr.
N.E.

615. **A new method for the estimation of inulin in plasma and urine.** H. Frank and F. Scheiffarth (Med. Univ. Klinik, Erlangen, Germany). *Klin. Wochschr.*, 1956, **34** (33–34), 914–918.—The method of Stöhr (*Hoppe-Seyl. Z.*, 1933, **222**, 261) for estimating fructose in blood has been adapted for inulin in blood or urine. To 2 ml of serum or of diluted urine (1:50) add 10 ml of water, 6 ml of $CdSO_4$ soln. (17·5 g of $CdSO_4.8H_2O$ dissolved in 84·6 ml of *N* H_2SO_4 and diluted to 500 ml with H_2O) and 2 ml of *N* NaOH, heat in boiling water for 10 to 15 min. and filter. To 2 ml of filtrate add 2 ml of Folin's tungstophosphoric acid reagent, mix by gentle shaking, heat in boiling water for 30 min. and then cool in running water for 5 min. Add 6 ml of *N* H_2SO_4, mix by shaking and read the colour at 700 mμ. An aliquot of standard soln. (100 mg of pure inulin per 100 ml in saturated aq. benzoic acid) is treated with each series of tests. For serum-inulin concn. of 1 to 40 mg-%, the extinction follows Beer's law and the colour is stable for 24 hr. Recovery of inulin added to serum and urine was 94 to 104%. H. F. W. Kirkpatrick

616. **The microbiological assay of inositol with a strain of *Schizosaccharomyces pombe*.** F. W. Norris and A. Darbre (Dept. of Appl. Biochem., The University, Birmingham, England). *Analyst*, 1956, **81**, 394–400.—The microbiological assay of total and free inositol by a tube method is described. The organism used is a strain of *Schizosaccharomyces pombe*. The basal medium (prep. described) is that described by Northam *et al.* (*J. Gen. Microbiol.*, 1952, **7**, 245) with the omission of asparagine and a twofold increase in biotin content. The procedures for the extraction of total inositol and free inositol and for the preparation of the inoculum are given. Sample and standard tubes containing the basal medium are sterilised, inoculated and incubated at 25° ± 0·2° for 72 hr. The turbidities are measured in a Spekker absorptiometer against the medium as blank. The free and total inositol contents of a number of food and other materials are given.
A. O. Jones

617. **Paper-chromatographic analysis of collagen and collagen derivatives.** J. M. Cassel (U.S. Nat. Bureau of Standards). *J. Amer. Leath. Chem. Ass.*, 1956, **51** (5), 223–234.—Eighteen amino acids were separated from hydrolysed collagen by two-dimensional chromatography, with the solvent mixture methanol - pyridine - water in one direction and, in the other, a mixture of *tert.*-butyl alcohol - ethyl methyl ketone - diethylamine - water. Individual amino acids were identified by the colour given when treated with ninhydrin. Spots were cut out, and the colour extracted in aq. propanol and determined spectrophotometrically. Good agreement is claimed with values given in the literature. B. R. Hazel

618. **The quantitative determination of acetol [hydroxypropanone].** C. G. Huggins and O. N. Miller (Dept. of Biochem., Tulane Univ. Sch. of Med., New Orleans, Louisiana, U.S.A.). *J. Biol. Chem.*, 1956, **221** (2), 711–718.—Two methods are described for the determination of hydroxypropanone (**I**). The first, a direct method, is based on the condensation of **I** with *o*-aminobenzaldehyde in alkaline solution at room temp. to give 3-hydroxyquinaldine, which is determined fluorophotometrically. The second, an indirect method, is based on the fact that **I** is converted into lactic acid by treatment with $CuSO_4$ - $Ca(OH)_2$. The lactic acid is determined colorimetrically; **I** is determined by difference after being destroyed by oxidation with HIO_4 before treatment with $CuSO_4$ - $Ca(OH)_2$. The indirect method gives somewhat higher results, usually about 15%. It distinguishes between **I** and acetoin and is perhaps more suitable for the determination of substrate levels of **I**.
J. N. Ashley

619. **Ionophoresis of nucleic acid components.** A. B. Foster, A. S. Jones and S. B. H. Rizvi (Chem. Dept., Univ., Birmingham, England). *Chem. & Ind.*, 1956, (35), 914–915.—The "enclosed strip" technique of electrophoresis (*cf. Chem. & Ind.*, 1952, 1050) was applied successfully to quant. analysis of nucleic acid components. A Whatman No. 3 paper was used with either 0·2 *M* acetate buffer (pH 3·5) or 0·2 *M* citrate buffer (pH 3·5) and voltage gradients up to 30 V per cm. Glass plates incorporating cooling systems enclosed the paper strip and, after each separation, these were carefully washed with H_2O and the washings made up to 25 ml. The extinction of these soln. at 260 mμ was invariably about 0·05, a value which corresponded to approx. 4% of that of the ribonucleic acid hydrolysate. The u.v. absorption spectrum of these washings revealed that the absorbing material did not originate from ribonucleic acid. This was confirmed by direct elution of a similar material from the paper itself and by recovery of 98·6% of the phosphorus as nucleotides after hydrolysis of purified commercial yeast ribonucleic acid and electrophoretic separation of the hydrolysate components. O. M. Whitton

620. **A sensitive method for the determination of ribonucleic acid in tissues and micro-organisms.** J. M. Webb (Lab. of Infectious Diseases, U.S. Dept. of Health, Educ. and Welfare, Bethesda, Maryland, U.S.A.). *J. Biol. Chem.*, 1956, **221** (2), 635–649.—A colorimetric method is described. Ribonucleic

acid is hydrolysed with 5% trichloroacetic acid, and the liberated ribose, in an aliquot of the hydrolysate, is heated with 4 *N* HCl saturated with NaCl. The furfuraldehyde so formed is extracted with xylene, and the extract is treated with *p*-bromophenylhydrazine in hydrochloric acid - ethanol to give a yellow colour (max. absorption at 450 mμ) which, under standardised conditions, is a measure of the amount of ribonucleic acid. The colour follows Beer's law from 9·4 to > 150 μg of purified ribonucleic acid. The method is more specific than the orcinol procedure because deoxyribonucleic acid does not interfere and the extraction with xylene minimises the effect of interfering substances.

J. N. ASHLEY

621. **The chemical composition of microsomes and mitochondria from silver beet. [Determination of ribonucleic acid and deoxyribonucleic acid.]** E. M. Martin and R. K. Morton (Dept. of Biochem., Univ. of Melbourne, Australia). *Biochem. J.*, 1956, **64** (2), 221–235.—Published methods for the determination of ribonucleic and deoxyribonucleic acids in plant materials are unsatisfactory, and those methods for ribonucleic acid based on the determination of ribose give high values. An improved method is described for the determination of these nucleic acids in plant material. It is based on hydrolysis of the dried desalted extracts of ribonucleic and deoxyribonucleic acid by 88% (v/v) formic acid and determination of the liberated purines and pyrimidines spectrophotometrically.

J. N. ASHLEY

622. **Colorimetric determination of histamine.** J. Baraud and L. Genevois (Lab. de Chim. Biol., Fac. des Sci., Bordeaux, France). *Bull. Soc. Chim. France*, 1956, (4), 681–683.—Histamine is extracted from the protein-free sample with amyl alcohol after removal of ether-soluble bases, etc., and is estimated colorimetrically with diazotised *p*-bromoaniline. *Procedure*—Protein is pptd. with trichloroacetic acid, and the solution, after being made alkaline, is extracted three times with ether (removing lipids, indoles and other bases). The aq. phase is then extracted three times with synthetic amyl alcohol (fermentation amyl alcohols may contain diazotisable substances), which extracts the histamine leaving glucides, phenols and histidine in the aq. phase. The histamine is then extracted with HCl and coupled with diazotised *p*-bromoaniline, and after 5 min. the red product is extracted into *iso*butyl alcohol where it is stable, and its absorption is measured at 546 mμ. This method is applied to normal and pathological blood and has a precision of ± 2%. E. J. H. BIRCH

623. **Quantitative determination of amino acids by fluorescence of derivatives on paper.** V. G. Shore and A. B. Pardee (Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1479–1481.—Amino acids on paper chromatograms are semi-quant. determined by spraying with xylose, heating and measuring the fluorescence of the spots. Good accuracy, between 5 and 10% error, may often be obtained. Application to insulin and β-lactoglobulin samples gave results in good agreement with those of other methods. G. P. COOK

624. **Application of paper micro-electrophoresis. V. Detection of enzymatic decarboxylation products of amino acids.** Fumio Hagihara (Pharm. Inst., Med. Faculty, Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (6), 613–615.—Detection of degradation products of arginine (**I**) and canavanine (**II**) with *Escherichia coli* No. 1 was studied by paper electrophoresis. The buffer soln. (pH 5·2) of the sample mixture is centrifuged, made pH 8·6 with barbitone buffer and submitted to electrophoresis (600 V, 1 mA per cm, 90 min.). The spots are revealed with sodium nitroprusside. **I** produces agmatine and **II** an unknown substance containing an *o*-guanidyl group. K. SAITO

625. **Investigations on rat serum albumin marked with tritium-labelled leucine. [Determination of tritium.]** J. Done and P. R. Payne (Human Nutr. Unit, Med. Res. Council Lab., Holly Hill, London). *Biochem. J.*, 1956, **64** (2), 266–274.—A routine assay of tritium is described. The combustion bomb method of production of gas for counting (Payne and Done, *Anal. Abstr.*, 1954, **1**, 2337) is used, followed by proportional counting as used by White *et al.* (*Brit. Abstr. C*, 1951, 241).

J. N. ASHLEY

626. **Identification and quantitative chromatographic determination of γ-aminobutyric acid on ion-exchange columns.** A. Waksman and E. J. Bigwood (Fac. Med., Brussels Univ., Belgium). *Ann. Acad. Sci. Fenn., AII*, 1955, **60**, 49–54.—This is an extension of the work of Moore and Stein (*J. Biol. Chem.*, 1951, **192**, 633). On the short 15-cm column used for the second chromatogram, good separation of γ-aminobutyric acid is not attained. This difficulty is overcome by using a 50-cm column of Dowex-50 with a citrate buffer of pH 4·9 as eluent. N. E.

627. **The semi-micro determination of sulphur in cystine and methionine.** T. T. Gorsuch (County Laboratories Ltd., Honeypot Lane, Stanmore, Middx., England). *Analyst*, 1956, **81**, 501–502.—In the method proposed, the organic S is oxidised and the resulting sulphate is reduced to H_2S. The material (≡ 1 to 2 mg of S) is boiled gently under a tilted reflux condenser for 2 hr. with 250 mg of $K_2Cr_2O_7$ and 2 ml of H_3PO_4. The cooled liquid is then treated with 10 ml of the reduction mixture (100 ml of HI of sp. gr. 1·7, 160 ml of conc. HCl and 30 ml of a 50% soln. of H_3PO_2, boiled for 2 min.). Delivery and exit tubes are fitted to the top of the condenser and the apparatus is swept out with N. The liquid is then boiled and the H_2S evolved is absorbed in ammoniacal cadmium acetate soln. The ppt. of CdS is washed with 5% acetic acid and collected. Its sulphur content is determined either by transferring the paper and ppt. to 25 ml of 0·1 *N* I soln. and titrating the excess of I with $Na_2S_2O_3$ soln. or by any other suitable method. A simultaneous blank determination is advisable. Results with cystine, methionine, sulphanilic acid and elementary S indicate satisfactory accuracy.

A. O. JONES

628. **Methods and limitations of chromatographic determination in protein hydrolysates.** F. Parisi, C. Palombi and G. Funes (Research Lab., Soc. "Distillerie Italiane," Milan). *Chim. e Ind.*, 1956, **38** (5), 398–403.—Methods for the identification and determination of protein amino-acids are developed and improved. The identification is performed with two-dimensional paper chromatography, and the determination of most of the amino acids by one-dimensional paper chromatography with buffered solvents. For the quant. determination of lysine, arginine and histidine, selective retention of amino acids on buffered

carboxylic resins is used; tyrosine and tryptophan have been determined in alkaline protein hydrolysates by u.v. spectroscopy. By these methods, deviations of only 2% are obtained. Analytical data obtained on pure amino-acid solutions and on *Saccharomyces cerevisiae* are presented. (74 references.) C. A. FINCH

629. **Chromatography of proteins. I. Cellulose ion-exchange adsorbents.** E. A. Peterson and H. A. Sober (Nat. Cancer Inst., Bethesda, Maryland, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 751–755.—Ion-exchange adsorbents that have a high capacity for the adsorption of proteins and permit of elution under mild conditions have been prepared from cellulose. One anion exchanger is prepared as follows. A suspension of wood cellulose (Solka-Floc; 60 g) in strong aq. NaOH (40 g in 170 ml) is allowed to stand, with occasional stirring, in an ice-bath for 30 min. Recrystallised 2-chlorotriethylamine hydrochloride (35 g) in water (45 ml) is added gradually. After thorough mixing, the mixture is immersed in an oil-bath at 80° to 85° for 35 min. and stirred occasionally. The product is cooled in an ice-bath and 2 *M* NaCl (250 ml) is added slowly. The thick suspension is filtered on a coarse sinter and the product is washed with *N* NaOH until the filtrate is no longer coloured. The resulting material is suspended in sufficient *N* HCl ($\simeq$ 350 ml) to give an acid suspension, which is immediately filtered, and the residue is successively washed with *N* NaOH (250 ml), *N* HCl (250 ml) and *N* NaOH (250 ml). Finally the cake is suspended in *N* NaOH (250 ml) then diluted with water (3 litres). After standing overnight, the supernatant liquor is decanted and the sediment is washed 5 or 6 times by decantation. The sediment is filtered off and washed with ethanol (3 × 500 ml). The dried product (45 g) contains 1·4% of N and has a good protein-adsorption capacity. The preparation of cation exchangers from Whatman cellulose powder is described.

II. Fractionation of serum protein on anion-exchange cellulose. H. A. Sober, F. J. Gutter, M. M. Wyckoff and E. A. Peterson. *Ibid.*, 1956, **78**, 756–763.—A description is given of the chromatographic analysis of serum proteins on the anion exchanger described in Part I. Gradients of salt concn. and pH were employed in elution. With decreasing pH and increasing salt concn., the protein components emerge in order of decreasing isoelectric point. The eluate fractions were examined by u.v. spectrophotometry and were characterised by electrophoresis. Good resolution was obtained with as much as 170 mg of material. C. A. SLATER

630. **A simple colorimetric micro-method for the determination of protein in biological material.** O.-S. Hinz (Univ.-Augenklinik, Hamburg-Eppendorf, Germany). *Klin. Wochschr.*, 1956, **34** (37–38), 1034.—The following method is recommended for determining protein in body fluids. Pipette 0·02 ml (or less) of cell-free protein soln. on to a small glass circle (15 mm diameter) and air dry. Fix and stain the protein by immersing for 10 min. in a soln. of Amido black 10B [5 g of dye suspended in 1 litre of glacial acetic acid - methanol (1:9) and allowed to stand for at least 48 hr., with occasional shaking, before use]. Wash in successive quantities of glacial acetic acid - methanol (1:9) until no further dye is removed, immerse the glass circle in 5 ml of 0·1 *N* NaOH and swirl gently until the dye is completely eluted. Measure the colour at 578 mμ and convert the reading to milligrams of protein per 100 ml of fluid by means of a factor determined with a standard protein soln. H. F. W. KIRKPATRICK

631. **Paper-disc electrophoresis. New device for separation of serum proteins.** N. C. Ganguli (Univ. Coll. of Sci. & Technol., Calcutta, India). *Anal. Chem.*, 1956, **28** (9), 1499–1501.—The simple apparatus shown is suitable for the separation of proteins from blood serum. The apparatus (illustrated) takes up to 12 samples at one time, applied at $<$ 1% concn. They are drawn out radially, the best separation being achieved after 4 hours' running at currents of 8 to 10 mA. E. G. CUMMINS

632. **Paper electrophoresis of the soluble proteins of the central nervous tissue.** R. Caravaglios and P. Chiaverini (Inst. of Gen. Path., Univ. of Pisa, Italy). *Experientia*, 1956, **12** (8), 303–304.—Brain and cerebellum (pooled separately), quickly dissected from ex-sanguinated albino rats of 200-g body weight, were frozen over solid CO_2 before being dispersed with 0·25 *M* sucrose (5 ml per g of tissue) in a homogeniser kept at freezing point. The suspension was centrifuged for 1 hr. at 2500 ***g*** in the cold, and the supernatant liquor was decanted and dialysed for 12 hr. at 2° with agitation, against several changes of water. After dialysis, the liquid was re-centrifuged at 2500 ***g*** for 1 hr. and freeze-dried. The dry material was dissolved in boric acid - Na_2SO_4 - NaOH buffer, pH 8·6, to give a final protein concn. of 10% (w/v). Electrophoresis was performed with a constant potential of $\simeq$ 6 to 8 V per cm for periods from 4 to 12 hr. After oven-drying the strips at 120° they were stained with Amido black 10B. The relative amounts of the components were determined by cutting the corresponding portions from the stained paper, eluting the dye with 5 ml of a 5% aq. phenol soln. and reading the extinction at 640 mμ. R. S. TONKS

633. **Application of a simple ion-exchange-resin technique to determination of serum or plasma protein-bound ^{127}I or protein-bound ^{131}I.** C. I. Slade (Dept. of Med., Univ. of California, San Francisco, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1956, **16** (8), 1122–1125.—Dowex 1 or Dowex 2 (X10, 200 to 400 mesh) prepared in the chloride form is used as an anion exchanger for removing inorganic iodide from plasma or serum. An aq. slurry of resin is drawn into 5·2-cm lengths of polyethylene tubing, previously closed at one end with glass wool, so as to form columns 3·5 cm long and 4 mm in diameter. The open ends of the tubes are then closed with glass wool and the prepared columns are stored in water. For use, the column casings are attached directly to syringes and the serum is either drawn through the column into the syringe, or if the syringe is previously filled it is expelled through the column. Samples measuring 2 to 4 ml were passed through the columns at flow rates of 6 to 10 or 4 to 6 ml per min., respectively. This procedure removed 99·6 to 99·8% of inorganic iodide in concn. of up to 10 mg per 100 ml of serum. H. F. W. KIRKPATRICK

634. **The quantitative measurement of γ-glutamyl transpeptidase activity.** E. G. Ball, J. P. Revel and O. Cooper (Dept. of Biol. Chem., Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Biol. Chem.*, 1956, **221** (2), 895–908.—The manometric method described is based on the uptake of CO that occurs in the presence of ferrous salts by the cysteinylglycine

liberated from glutathione by the enzyme. Another method for determination of the enzyme activity depends on the ability of alloxan to react with glutathione to form a compound with max. absorption at 305 mμ. This method measures the disappearance of glutathione from the reaction mixture. The two methods give concordant results under a variety of conditions. J. N. ASHLEY

635. **Elution chromatographic separation of free and esterified cholesterol in organ and serum fats and direct colorimetric estimation.** H. Schön and F. Gey. *Hoppe-Seyl. Z.*, 1956, **303** (1–2), 81–90.—By passing a light-petroleum extract of the lipids through an alumina column (35 cm × 1·2 cm) and subsequent elution with various concn. of diethyl ether in light petroleum, separation into free cholesterol, triglycerides and esterified cholesterol is achieved. If the triglyceride content is not high, then free cholesterol and triglycerides may be obtained as one fraction and esterified cholesterol as the other. The triglycerides will not interfere with the subsequent colour reaction. *Procedure*—Dissolve the fat extract from 0·1 to 0·5 ml of serum or 5 to 15 mg of liver fat or 5 to 20 mg of sebum in 5 ml of light petroleum and pour through the column so as to pass about 3 ml per min. Elution with 75 ml of 4% (v/v) ether in light petroleum gives the cholesterol. Follow this with 75 to 100 ml of 40% (v/v) ether in light petroleum and the fraction containing both free cholesterol and triglycerides will be obtained. Wash the column with 25 ml of 50% ether in light petroleum to ensure that it is free from cholesterol. Details are also given of a technique for separating the triglycerides as a distinct fraction. The eluates are distilled from a glycerol bath and the residues dried in a vacuum-desiccator. If there is any delay before colour development the residue should be kept in an atmosphere of N. Dissolve the residue in 3 ml of $CHCl_3$ and add 2 ml of a freshly prepared mixture of 20% $ZnCl_2$ in acetic acid and acetyl chloride (2:1, v/v). Stopper and set aside for 3 hr. in the dark. Then add 4 ml of $CHCl_3$ to make the final vol. 10 ml, and read against the reagent blank at 520 mμ. The colour remains constant for a further 2·5 hr. Beer's law is obeyed at concn. ranging from 0·2 to 100 μg per ml. The max. error is ± 2% for esterified cholesterol and ± 5% for free cholesterol. All reagents should be free from peroxides. F. POWELL

636. **The fractionation of steroids by paper chromatography.** G. W. Oertel (Lab. Byk-Gulden Lomberg, Chem. Fabrik G.m.b.H., Konstanz). *Naturwissenschaften*, 1956, **43** (1), 18.—The steroids are chromatographically concentrated into a small filter-paper tongue. This tongue is cut off and inserted into a new strip a few centimetres above the fluid level of a formamide - *n*-hexane - benzene mixture. Ascending chromatography separates the steroids, some migrating with the solvent front. The top of the strip is cut to form a tongue and made to project through a slot in the lid where it is transfixed by a platinum wire. As soon as the solvent front reaches the projecting paper a current of warm air is turned on to evaporate the solvent. In this manner all the steroid material travelling with the solvent front is concentrated in the small paper tongue. In a 4-hr. run it is found that with 50-μg samples all the C_{19} steroids have been moved to the tip of the strip, whereas all the C_{21} steroids have remained in the inserted piece of paper near the origin. E. KAWERAU

637. **A simple and rapid method of determining urinary 17-hydroxycorticosteroids: Reddy's method.** J. Hertoghe, F. Stein and P. Osinski (Medical Clinic, Univ. of Louvain, France). *Ann. Endocr., Paris*, 1955, **16**, 962–968.—The method of Reddy (*Metabolism*, 1954, **8**, 489) has been studied and found to be simple, rapid and reliable provided that a correction of the Allen type is made to eliminate the error due to certain non-specific colour-development effects (*cf.* Hertoghe and Crabbe, *Acta Clin. Belg.*, 1955, **10**, 369, 397). The applications of the method to clinical and expt. work is illustrated by a series of examples. H. F. W. KIRKPATRICK

638. **Determination of urinary 17-hydroxycorticosteroids.** P. O. Tommasino, J. J. Staffieri and R. R. Berli. *Act. Bioquím., Santa Fé*, 1956, **5** (1), 3–5.—A 24-hr. urine sample is stored at 0° to 4° during collection and analysed within 24 hr. from its completion. Depending on the 17-hydroxycorticosteroid content, 5 to 20 ml is acidified to pH 1 with 50% H_2SO_4 and extracted twice with 0·5 vol. of butanol, emulsions formed being broken by centrifuging. The combined extracts are washed with 0·2 vol. of 0·1 *N* NaOH and 0·2 vol. of 0·01 *N* H_2SO_4. A series of colorimetric determinations are made to measure the colour formed when 1 ml of extract is treated with 4 ml of a reagent consisting of 65 mg of phenylhydrazine in 100 ml of 62% (v/v) aqueous H_2SO_4. The series of determinations eliminates colour formed between the reagent and butanol, and between H_2SO_4 and the extract and butanol, and also measures the colour formed with a standard cortisone solution. This permits the 17-hydroxycorticosteroid content of the original urine to be calculated. D. LEIGHTON

639. **Characterisation of 17-ketosteroids by derivatives formed in the Zimmermann reaction.** A. E. Kellie and E. R. Smith (Courtauld Inst. of Biochem., Middlesex Hospital Med. School, London). *Nature*, 1956, **178**, 323.—The deriv. formed from 17-ketosteroids by the Zimmermann reaction are separated by paper chromatography with a hydrocarbon - aq. methanol system. The spots are located by viewing in u.v. light, or by treatment with ethanolic KOH. A table is given of the R_F values of the free 17-ketosteroids and their deriv., also a list of Zimmermann steroid complexes that cannot be separated under the described conditions. G. S. ROBERTS

640. **Interfering chromogens in the 17-ketosteroid determination.** L. N. Antunes (Rua Potiguar Medeíros 99, Pinheiros, São Paulo, Brasil). *J. Clin. Endocrin. & Metabolism*, 1956, **16** (8), 1125–1126.—The addition of formaldehyde to urine before acid hydrolysis results in perfectly colourless ether extracts that yield values for ketosteroids determined by the Zimmermann reaction in satisfactory agreement with those obtained with untreated extracts; 1 ml of soln. (40% formaldehyde soln. diluted 1 to 5 with water) is sufficient to prevent colour contamination of 50 ml of urine. H. F. W. KIRKPATRICK

641. **Diagnostic test for cancer.** A. A. Hakim (Med. Res. Dept., Nat. Children's Cardiac Hosp., Miami, Florida, U.S.A.). *Experientia*, 1956, **12** (8), 313–314.—An abnormal acetate-lipid has been demonstrated in serum from human cancer cases by a modified Feulgen reaction. In patients with carcinoma the test is 100% positive. Out of 100 normal persons only two gave positive reactions.

To 500 μl of serum, the following reagents are added in the order given—10 μl of 0·5% ascorbic acid, 20 μl of 0·5% thiamine hydrochloride, 100 μl of 95% alcohol, 150 μl of 10% KOH, 100 μl of 0·5% $CuSO_4$ and 120 μl of 0·02% fuchsine (basic). Mix well after each addition. The colour is read in sunlight after 15 to 30 min. Normal serum gives a red colour whilst serum from tumour-bearing patients gives a purple colour. R. S. TONKS

Drugs

642. **Paper-chromatographic separation of alkaloids.** Y. T. Sun [Nat. Taiwan Univ., Taiwan (Formosa)]. *J. Taiwan Pharm. Ass.*, 1954, **6**, 17–20.—The use of acid solvent in the paper chromatography of strychnine (**I**), brucine (**II**), pilocarpine (**III**) and pilosine (**IV**) did not give good results (*cf.* Munier, *Bull. Soc. Chim. Biol.*, 1951, **33**, 846) and the difficulty was solved by this work. Whatman paper No. F (10 cm × 46 cm) moistened with KH_2PO_4 soln. (**V**) was used with descending technique and the results were (concn. of **V**, solvent, and R_F values given)—0·2 *M*, butanol, **I** 0·42, **II** 0·32; 0·2 *M*, *sec.*-butyl alcohol, **I** 0·36, **II** 0·23; 0·2 *M*, *tert.*-butyl alcohol - H_2O (3:1), **I** 0·72, **II** 0·61; 0·2 *M*, propanol - H_2O (3:1), **I** 0·69, **II** 0·55; 0·5 *M* *iso*propyl alcohol - H_2O (3:1), **I** 0·63, **II** 0·49; 1 *M*, butanol, **I** 0·27, **II** 0·16; 1 *M*, *sec.*-butyl alcohol, **I** 0·31, **II** 0·20; 1 *M*, *iso*propyl alcohol - H_2O (3:1), **I** 0·68, **II** 0·57; 0·1 *M* *iso*propyl alcohol - H_2O (3:1), cocaine (**VI**) 0·80, pseudococaine (**VII**) 0·87, tropacocaine (**VIII**) 0·84; 0·2 *M*, *iso*propyl alcohol - H_2O (3:1), **VI** 0·68, **VII** 0·77, **VIII** 0·72; 0·2 *M*, *iso*butyl alcohol, **VI** 0·36, **VII** 0·66, **VIII** 0·36; 1 *M*, butanol, **VI** 0·39, **VII** 0·70, **VIII** 0·41; 1 *M*, *sec.*-butyl alcohol, **VI** 0·44, **VII** 0·78, **VIII** 0·40. The R_F values obtained for **III** and **IV** were: 0·375 *M*, $Ca(H_2PO_4)_2$, *sec.*-butyl alcohol, **III** 0·14, **IV** 0·25; 0·375 *M* $Ca(H_2PO_4)_2$, propanol - H_2O (3:1), **III** 0·35, **IV** 0·40; 0·5 *M* **V**, propanol - H_2O (3:1), **III** 0·41, **IV** 0·48. CHEM. ABSTR.

643. **The use of sodium tetraphenylboron as a means of identifying and isolating alkaloids.** W. E. Scott, H. M. Doukas and P. S. Schaffer (Eastern Regional Res. Lab., Dept. of Agric., Philadelphia, Pa., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 568–570.—The sensitivities of sodium tetraphenylboron (**I**) and Mayer's reagent (**II**) towards 34 alkaloids are compared. In all cases, **I** is at least as good as **II**, although it has the disadvantage of pptg. K^+ and NH_4^+. The complexes of **I** with 21 alkaloids have been isolated, and their m.p. are tabulated. In many cases the alkaloid can be recovered in good yield by gentle heating on a water bath in acetone or ethanol with 5% NaOH for 15 min., removal of the solvent and extraction with $CHCl_3$. A. R. ROGERS

644. **The determination of small quantities of alkaloids using potassium iodobismuthate. III.** W. Poethke and H. Trabert. *Pharm. Zentralh.*, 1955, **94** (11), 432–439.—The methods described in a previous publication (*Anal. Abstr.*, 1956, **3**, 808) are applied to the assay of atropine in ampoules, eye ointment, pills and extracts of belladonna, and in tablets and stomach powders containing belladonna, and of strychnine in ampoules, pills and granular preparations. Good results were obtained when assaying comparatively small amounts of the alkaloids. P. S. STROSS

645. **The polarographic determination of morphine in poppy capsules.** S. Pfeifer and W. Keller (Pharmaz. Inst. Humboldt Univ., Berlin, Germany). *Pharm. Zentralh.*, 1956, **95** (5), 189–193.—The determination of morphine by polarography of its nitroso derivative is described. By following the extraction procedure described, the interference of all constituents of poppy heads, except narcotoline, which interferes only to a minor extent, is avoided, only 0·3 g of sample is used, and the whole determination takes 45 min. Triturate the finely powdered dry poppy capsule (0·3 g) with 1 ml of water and 7 to 8 g of "acid" alumina and introduce into a glass column about 2 cm in diameter which already contains 4 g of alumina. Percolate with water (20 ml) during 20 min. To the extract, add HCl (3·5 ml) and dilute to 25 ml. To 5 ml add *N* $NaNO_2$ (2 ml) and, after exactly 5 min., NaOH [20% (w/v)] (3 ml) and gelatin solution (7 drops). Bubble N through the soln. during 5 min. and polarograph. Calculate the morphine content from a calibration curve. P. S. STROSS

646. **A chromatographic method of assaying morphine in opium.** Chih-Kuei Liang. *J. Taiwan Pharm. Ass.*, 1955, **6**, 11–14.—Chromatographic analysis showed that morphine (**I**) obtained by the Liang method (*cf.* ST/SOA/SER.K/18, United Nations) still contains some impurities, including phenolic alkaloids in not more than 0·1 to 0·2% quantity. The acidic opium extract was made alkaline, treated with a small amount of Na_2SO_3, and extracted with ether to remove non-phenolic alkaloids. The alkaline soln. was neutralised, made alkaline with aq. NH_3, extracted with a saturated soln. of NH_3 in $CHCl_3$ - butanol mixture (95:5), and chromatographed on ammoniated silica gel. The column was then eluted with $CHCl_3$ - butanol (80:20) saturated with NH_3, the solvents were distilled off, and **I** was titrated with acid or determined by its optical rotation. CHEM. ABSTR.

647. **Colorimetric determination of codeine.** Shichiro Akiya, Yasuo Nakazawa and Shunji Ishikura (Pharm. Inst., Med. Faculty, Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (5), 608–610.—Codeine is extracted with chloroform from a basic soln. and oxidised with 5% $KMnO_4$ to produce formaldehyde, which is colorimetrically determined with chromotropic acid and H_2SO_4 at 580 mμ. In the presence of lactose or sucrose, the sample is treated with *N* HCl on a boiling-water bath (for the hydrolysis of the saccharide). When the $CHCl_3$ extraction is carried out from 10% NaOH, morphine (which undergoes a similar reaction) remains in the aq. layer. The extract is evaporated to dryness, dissolved in 10% HCl (1 to 10 ml, to produce a soln. containing 30 to 200 μg of codeine per ml) and a portion is treated with the $KMnO_4$ (0·2 ml) at room temp. for 10 min., then with Na_2SO_3 (25%, 0·2 ml), ice-cooled and mixed with one drop of 1% chromotropic acid and conc. H_2SO_4. The product is kept in a water bath for 15 min. and the extinction is measured. K. SAITO

648. **A source of error in the assay of strychnine salts and preparations containing strychnine.** A. C. Caws and G. E. Foster (Wellcome Chem. Works, Dartford, Kent). *J. Pharm. Pharmacol.*, 1956, **8** (10), 790–798.—In the standard procedure for the assay of strychnine (**I**) salts, the volumetric method gives low results and the gravimetric method high results. This is attributed to conversion of part of

the **I** into a chloro compound (**II**) by reaction with hot $CHCl_3$. **II** has been isolated but not identified; it is not **I** hydrochloride; it is dextrorotatory and part but not all of the Cl is ionised. The error in the assay can be eliminated by titrating the recovered alkaloid in glacial acetic acid with standard $HClO_4$, or by shaking the $CHCl_3$ extract with excess of standard aq. H_2SO_4 and back-titrating with standard aq. NaOH. The formation of **II** does not affect the absorptiometric estimation of **I** by the Malaquin or the ammonium vanadate reactions. A. R. ROGERS

649. **A colorimetric method for the estimation of strychnine and brucine in nux vomica by the use of ammonium reineckate.** M. Karmazín and J. Böswart (ForschInst. f. Heilpflanzen, Prague, Czechoslovakia). *Pharm. Zentralh.*, 1956, **95** (1), 10–14.—Strychnine and brucine are pptd. as their reineckates, which are dissolved in acetone and the extinction at 525 mμ is measured. The alkaloids are extracted from the sample by the method of the D.A.B.VI, with peroxide-free ether - chloroform (2:1). To an ice-cold aliquot representing 0·4 g of sample in 1% H_2SO_4 add satd. ammonium reineckate soln. (3 ml) and allow to stand in an ice bath for exactly one hour. Separate the ppt. on a No. 4 sintered-glass filter and wash twice with 5 ml of a soln. containing 2 ml of satd. ammonium reineckate soln. in 1 litre of water. Dissolve the ppt. in acetone and dilute to 10 ml. Measure the extinction at 525 mμ and calculate the alkaloid content from a calibration curve obtained by using a mixture of equal quantities of strychnine and brucine. P. S. STROSS

650. **Determination of the alkaloids of ergot of rye (*Claviceps purpurea* Tul.).** R. Paris and R. Stauber (Faculté de Pharm. de Paris, Lab. de Matière Méd.). *Ann. Pharm. Franç.*, 1955, **13** (12), 731–735.—Various methods for the separation and determination of the alkaloids of ergot of rye are reviewed, and certain methods selected. The solution of Allport and Cocking (B.P. 1953) (*p*-dimethylaminobenzaldehyde - $FeCl_3$ reagent) is shown to give variable results until 6 days after preparation, but is stable from this time for 3 months, and the blue colour formed in the reaction is stable for 8 hr. at 20°. For the separation of complex mixtures the method of Strong and Maurina (*J. Amer. Pharm. Ass.*, 1953, **42**, 414) is preferred; in this, ergotamine-type alkaloids are extracted with CCl_4 and the ergometrine and ergobasine type are salted out and extracted with ether. For the analysis of an ergot powder, a micro-method is considered more suitable than the National Formulary method, which is applicable only to samples >2 g. The powder (0·1 g) is weighed into a brown stoppered bottle and degreased 3 times for 1 hr. with 5 ml of light petroleum. The light petroleum is decanted and last traces are evaporated off; 5 ml of a solution of 2 ml of 10% aq. NH_3 in 120 ml of ether is shaken with the residue for 2 hr. A 3-ml portion of the ether solution is concentrated and added to 3 ml of 1% (w/v) H_2SO_4. The ether is removed and 6 ml of *p*-dimethylaminobenzaldehyde reagent is added and the total alkaloid determined colorimetrically. The standard error of test experiments was ± 6 mg in 123 mg on degreased powder and ± 6·4 mg in 120 mg on undegreased powder. E. J. H. BIRCH

651. **The determination of the base content and acid component of ergotoxine phosphate in anhydrous and differential solvents, respectively.** I. Gyenes (Pharm. Factory of Kőbánya, Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 239–241.—Phosphate is titrated with K methoxide (**I**) in a differential solvent as KH_2PO_4 (**II**). *Procedure*—To determine the base content of ergotoxine phosphate (**III**), dissolve 100 to 150 mg in acetic acid (20 ml, containing not more than 2% of H_2O) and add 1 drop of crystal violet in acetic acid (0·1%). Titrate to the first (blue) colour-change with 0·05 *N* $HClO_4$ in acetic acid, which has been standardised against diphenylguanidine. During titration, keep the temp. const. to within ± 0·5°. The probable limit of error is ± 0·7%. The phosphate content of **III** is determined by dissolving (with warming, if necessary) 150 to 200 mg of sample in pyridine (5 ml) neutralised against azo violet. Add acetone (20 ml) previously neutralised with 0·1 *N* **I** in the presence of azo violet (0·5 ml per 50 ml of solvent) and titrate to orange - red with 0·1 *N* **I**. The soln. becomes cloudy at first, but near the end-point the **II** settles out. The probable limit of error is ± 0·5%. A. G. PETO

652. **The separation, micro-estimation and distribution of the alkaloids of hemlock (*Conium maculatum* L.).** B. T. Cromwell (Dept. of Botany, Univ. of Hull, England). *Biochem. J.*, 1956, **64** (2), 259–266.—Methods are described for the determination of the individual alkaloids in *Conium maculatum*. The alkaloids are isolated by steam-distillation. γ-Coniceine is determined in the presence of the other alkaloids by the nitroprusside reaction. This alkaloid gives a red colour with sodium nitroprusside and Na_2CO_3; the intensity of the colour is determined with an absorptiometer. Over the range of 20 to 200 μg the extinction is proportional to the concn. of γ-coniceine. The other steam-volatile alkaloids, coniine, *N*-methylconiine and conhydrine are separated by paper chromatography and, after elution, each is treated with bromothymol blue to give a yellow compound which is soluble in benzene. The intensity of the colour is determined in an absorptiometer. J. N. ASHLEY

653. **Sabadilla alkaloids. VI. Separation of veratridine and cevadine by countercurrent distribution. pH *vs.* partition coefficients.** H. Mitchner and L. M. Parks (Univ. of Wisconsin, Sch. of Pharmacy, Madison, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 549–555.—Contrary to a previous report (*cf. Anal. Abstr.*, 1955, **2**, 439), it has now been found that both cevadine (**I**) and veratridine (**II**) behave ideally in partition studies. Countercurrent distribution with a $CHCl_3$ - citrate buffer of pH 3·95 can be used to separate **I** and **II** in a high state of purity in a relatively small number (≃ 30) of transfers. The benzene - phosphate buffer system of pH 5·85 needs a much larger number (≃ 300) of transfers. Chromatographic studies with the latter system on a silicic acid column showed that adsorption as well as partition was involved. The ratio of the extinctions at 218 mμ and 293 mμ may be used to check the purity of **II** or to determine small amounts of **I** present as an impurity in **II**. $E_{218}:E_{293} = 3{\cdot}50 \pm 0{\cdot}03$ for pure **II**. **I** and **II** in benzene soln. can be determined by non-aqueous titration with 0·01 *N* $HClO_4$ in glacial acetic acid, with quinaldine red as indicator (end-point, red to colourless). For the titration of **I** or **II** in $CHCl_3$ soln., the addition of an equal vol. of Skelly C to the soln. before titration sharpens the end-point and reduces the blank value. A. R. ROGERS

654. **Determination of reserpine.** C. R. Szalkowski and W. J. Mader (Merck. & Co. Inc., Rahway, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (9), 613–617.—Reserpine, reserpic acid, methyl reserpate and rescinnamine solutions develop a greenish-yellow fluorescence with max. extinction at 388 to 390 mμ when treated with H_2SO_4 and $NaNO_2$. The extinction, when developed under standard conditions, conforms to Beer's law and can be used for the determination of reserpine in extracts from tablets, elixirs and solutions. Reserpine can be separated from reserpic acid by $CHCl_3$ extraction from acid solution. Similar alkaloids do not interfere with the determination. The method is applicable in the presence of many formulation ingredients, but certain others such as mannitol hexanitrate, phenacetin and theophylline inhibit the colour formation. The recovery of reserpine from known mixtures of reserpine, lactose, starch and magnesium stearate ranged from 97 to 101%. K. A. PROCTOR

655. **The evaluation of digitalis by circular paper chromatography.** K. H. Boltze and G. Wendschuh (Pharmacol. Inst. Friedrich-Schiller Univ., Jena, Germany). *Pharm. Zentralh.*, 1956, **95** (3), 96–102.—A simple apparatus suitable for paper chromatography of digitalis preparations on circular filter-papers is described in which a chloroform - water - alcohol or xylene - ethyl methyl ketone - formamide solvent system is used. The bands are developed by spraying with a chloroform soln. of $SbCl_3$ or trichloroacetic acid, drying at 110° and viewing in daylight and u.v. light. Impurities and gitoxin in commercial digitoxin can be detected. Chromatography of digitalis tinctures after purification with lead acetate gave a number of unidentified bands as well as those of gitoxin and digitoxin. P. S. STROSS

656. **The comparative investigation by fluorimetry of the glycosides of *Digitalis lanata*.** I. Gyenes (Chem. Works Gedeon Richter Ltd., Budapest, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 267–279 (in English).—A method is described for the fluorimetric estimation of lanatoside B (**I**), expressed as gitoxin (**II**), in impure lanatoside C and in lanatoside A + B + C, and of **II** in impure digitoxin. Measurements are made in syrupy H_3PO_4 - propane-1:2-diol (4:3) soln. with a Pulfrich fluorimeter (filter L3). Air is removed from the soln. by heating in a vacuum before the measurement is made. The presence of lanatoside C alters the standard curve of **II**, as it forms a yellow colour. The percentage of **I** or of **II** in numerous samples of digitoxin and the lanatosides has been measured with a probable error of 0·1 to 0·4% of **II**. A. R. ROGERS

657. **The chemical assay of cascara.** A. A. J. Fluck, W. Mitchell and S. A. Wood (Stafford Allen & Sons Ltd., Wharf Road, London). *J. Pharm. Pharmacol.*, 1956, **8** (10), 781–788.—The chemical method of Fairbairn and Mahran (*J. Pharm. Pharmacol.*, 1953, **5**, 827) for the assay of dry extract of cascara has been found to be unreliable; the presence of H_2O_2 during hydrolysis causes partial destruction of anthraquinones and it also appears to liberate additional anthraquinone-like material. A variety of methods has been studied. Alkaline hydrolysis destroys most of the aglycones. Hydrolysis of aloe-emodin with aq. HCl causes less loss than hydrolysis with aq. H_2SO_4. Prolonged hydrolysis in the cold gives relatively pure aglycones, but could not be used in a practicable assay method. Light petroleum effects selective extraction of the aglycones, but complete extraction requires very large volumes. A method involving hydrolysis with boiling aq. HCl, extraction with benzene and partition chromatography on silica gel containing 15% of H_2O with C_6H_6 - $CHCl_3$ (9:1) as eluent gave relatively pure aglycones, but the quant. results were variable and the method is not recommended. A. R. ROGERS

658. **Improvements in the spectrophotometric determination of santonin.** Tadayuki Okuma, Yutaka Kimura and Hiroshi Murayama (Taisho Pharm. Co. Ltd., Takata-minami-cho, Toshima-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (6), 742–743.—The colour produced by santonin (**I**) with 2:4-dinitrophenylhydrazine in ethanolic NaOH (Yamaguchi *et al.*, *Ibid.*, 1952, **72**, 581; 1953, **73**, 264) is unstable and the soln. readily becomes turbid; the use of a mixture of aq. NH_3 soln. (28%) and acetone (1 + 1) is suggested in place of NaOH. The extinction at 500 mμ is proportional to the concn. of **I** (2 to 25 mg per ml) and remains unchanged for > 1 hr. K. SAITO

659. **Polarographic determination of testosterone, methyltestosterone, progesterone and riboflavine** M. Sterescu and S. Negritescu. *Revista de Chimie*, 1956, **7** (3), 159–162.—The ketosterols are determined polarographically in aq. ethanolic soln. at pH 5·5 with 0·1 *N* LiCl as the supporting electrolyte. For methyltestosterone, $E_{\frac{1}{2}}$ is −1·55 V and for progesterone and testosterone −1·58 V, both *vs.* the S.C.E. Riboflavine is determined after dissolving the sample in aq. 5% sodium salicylate soln.; $E_{\frac{1}{2}}$ is −0·44 V *vs.* the S.C.E. The methods are applied to the determination of methyltestosterone in pills and of riboflavine in pills and ampoules. J. H. WATON

660. **The microbiological assay of vitamin B_{12} in liver extracts. I. Experimental design and problems of validity.** F. A. Robinson, M. E. H. Fitzgerald and J. J. Grimshaw (Allen and Hanburys Ltd., Ware, England). *J. Pharm. Pharmacol.*, 1956, **8** (9), 635–647.—Experimental methods are given for the determination of cobalamins in liver extracts by means of plate assay methods with *Escherichia coli* 8134 and plate and tube assay methods with *Lactobacillus leichmannii* 7854. Fourteen samples of liver extracts have been assayed by each of five methods. Significant departures from linearity may occur in the dose - response curve of the test soln., and a (3,3) design should be used. It is considered that the titrimetric tube assay in which *Lb. leichmannii* with the U.S.P. medium is used is the most reliable method of estimating the vitamin-B_{12} content of liver extracts. A. R. ROGERS

661. **Chromatographic determination of insulin potency. II. Standard curve for measurement.** Yuichi Sasano and Katsumi Higashi (Tokyo Res. Lab., Taiyo Fisheries Co. Ltd., Nishi-12, Tsukishima, Chuo-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (2), 213–214.—Comparison between the potency of insulin determined by the paper-chromatographic method (Asaoka *et al.*, *Anal. Abstr.*, 1956, **3**, 2261) and that by the bioassay was made by the use of a standard curve obtained with crystalline insulin. They show an agreement within ± 0·7%. K. SAITO

662. **Determination of penicillin by nitrometry.** Masatoshi Nagawa and Hideyo Shindo (Takamine Res. Lab., Sankyo Co. Ltd., Nishi-shinagawa, Shinagawa-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (1), 101–102.—Penicillin (**I**) is converted into penicillamine (**II**) and penilloaldehyde (**III**) by the action of caustic alkali. **III** is hydrolysed to aminoacetaldehyde (**IV**); from 1 mol. of **I**, two amino groups are thus produced, which are determined nitrometrically. The sample is heated at 60° for 10 min. with *N* NaOH, diluted and again heated on a boiling-water bath for 1 min. with 3 *N* HCl. A portion of the cooled acid soln. is neutralised with 25% Na acetate and submitted to nitrometry (Yamagishi *et al.*, *Ibid.*, 1954, **74**, 278).

K. Saito

663. **The decomposition of penicillin preparations: the determination of penicilloic acid.** I. Flóderer and E. [Mrs. S.] Farkas (United Pharm. and Foodstuff Factory, Budapest). *Magyar Kém. Foly.*, 1956, **62** (6), 209–211.—As it was suspected that the decomposition of penicilloic acid (**I**) causes the yellow colour of penicillin potassium, Pan's method (*Anal. Chem.*, 1954, **26**, 1438) was modified for the determination of **I**. Penicillin was extracted with $CHCl_3$ from an aq. soln. buffered to pH 4·8 with an $(NH_4)_2SO_4$ - saturated phosphate - citrate buffer. The **I** remaining in the soln. was determined by Nelson's method (*J. Biol. Chem.*, 1944, **153**, 375). The sensitivity is 0·1 to 0·2%. In the iodimetric determination of penicillin, **I** consumes iodine in the blank titration, hence the value obtained is too low. Samples containing **I** absorb 2 to 3 times more water (5 to 6% in 24 hr. at 70% r.h.) than pure samples.

A. G. Peto

664. **Metal chelate compounds of tetracycline derivatives. IV. Colorimetric determination of chlortetracycline in urine by cation-exchange resin adsorption and formation of its borate complex.** Takeichi Sakaguchi and Akira Hanaki (Pharm. Faculty, Chiba Univ., Inohana-cho, Chiba). *J. Pharm. Soc. Japan*, 1956, **76** (2), 172–175.—Chlortetracycline (**I**) (< 1 mg) is adsorbed on a column of Amberlite IR-112 (H) and eluted with warm *N* HCl in 80% ethanol (100 ml) and determined by the borate complex method (*cf.* Sakaguchi, *Anal. Abstr.*, 1956, **3**, 520). Other ingredients in urine (25 ml) are successively eluted with water (100 ml), 0·3 *N* HCl (30 ml), 1·5 *N* acetic acid in ethanol (30 ml) and 0·2 *N* HCl in ethanol (20 ml), before the elution of **I**. **I** in the eluate is evaporated to dryness, dissolved in water (0·4 ml), made up to 10 ml with boric acid (10% H_3BO_3 in conc. H_2SO_4, 2 ml) and conc. H_2SO_4, and the extinction is measured at 530 mμ after 2 hr.

K. Saito

665. **Determination of chloramphenicol by nitrometry.** Masatoshi Nagawa and Hideyo Shindo (Takamine Res. Lab., Sankyo Co. Ltd., Nishi-shinagawa, Shinagawa-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (1), 99–100.—Chloramphenicol is dissolved in 4% HCl and heated on a boiling-water bath. The resulting D(−)-threo-2-amino-1-*p*-nitrophenylpropane-1:3-diol (1-base) is introduced into a nitrometer with Na acetate (25 g in 100 ml of water, 0·5 ml), acetic acid (1 ml) and saturated NaCl soln. (5·5 ml). The small amount of amino N is determined by the successive action of $NaNO_2$ (15 g in 20 ml of water, 0·5 ml), NaOH (10 *N*, 2 ml) and $KMnO_4$ (saturated soln. in saturated NaCl) (*cf.* Yamagishi *et al.*, *Ibid.*, 1954, **74**, 278).

K. Saito

666. **Polarographic determination of chloral.** J. Barlot and C. Albisson (Lab. de la Poudrerie Nat. de Toulouse, France). *Chim. Anal.*, 1956, **38** (9), 313–315.—Reduction of chloral in acid media results in the production of a many-stepped wave which is difficult to interpret. In the present method, the aldehyde radical is converted into the oxime, which gives two distinct waves of reduction at a very low potential. The total duration of the method is 2 hr.

C. A. Slater

667. **A study of a radiometric analysis of phenobarbital [phenobarbitone.]** M. Pikoff and J. E. Christian (Bio-nucleonics Lab., Purdue Univ., Lafayette, Ind., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (9), 623–625.—A radioactive determination of phenobarbitone with ^{203}Hg as the labelling isotope is described. By this method phenobarbitone may be determined at levels ranging from 1 to 200 μg. The radioactive derivative is prepared by a chromatographic procedure and then determined by a "carrier method" or "direct method", both of which have the same degree of accuracy and precision. Levels as low as 12·5 μg were analysed with errors of ± 7% and levels of 1 μg with errors of ± 25%. The method is only applicable to the analysis of barbiturate samples that are free from impurities and that react with Hg to form insoluble substances.

K. A. Proctor

668. **The characterisation of some local anaesthetics.** E. Hannig and W. Karau (Pharmacol. Inst. Univ. Halle-Saale, Germany). *Pharm. Zentralh.*, 1956, **95** (5), 187–189.—The identification of Falicain (β-piperidinoethyl 4-propoxyphenyl ketone) hydrochloride, procaine, amethocaine and lignocaine by pptn. of their salts with disulphonylamines is described. The melting points of the compounds formed with 4:4′-diaminodiphenyldisulphonylamine, 4:4′-dichlorodiphenyldisulphonylamine and 3:4:3′:4′-tetrachlorodiphenyldisulphonylamine are characteristic, but the method was found to be unsuitable for quantitative work.

P. S. Stross

669. **The analytical behaviour of chlorprocaine.** M. Hädicke (Staatl. Inst. Arzneimittelprüfung, Jena, Germany). *Pharm. Zentralh.*, 1955, **94** (10), 384–388.—Chlorprocaine may be distinguished from procaine by its m.p. and by the crystal formation (illustrated) of the ppt. with flavianic acid, reinecke salt and dilituric acid. A bromimetric procedure or pptn. as reineckate may be used for its determination.

N.E.

670. **Analysis of drugs and chemicals by paper electrophoresis. III. Separation and identification of salicylic acid and its derivatives.** Yahyoe Kinoshita and Shigetaka Moriyama (Pharm. School, Nagoya City Univ., Tanabe-cho, Mizuho-ku, Nagoya). *J. Pharm. Soc. Japan*, 1956, **76** (6), 709–712.—Electrophoresis (400 V, 1 mA per cm, 60 min.) of salicylic acid (**I**), acetylsalicylic acid (**II**), phenylsalicylic acid (**III**), 4-aminosalicylic acid (**IV**) and salicylamide (**V**) was studied in various buffer soln. of pH 2 to 10. **I**, **II** and **IV** migrate towards the anode, and **V** towards the cathode at pH < 8·0; **III** remains at the initial point whatever the pH. The R_F values of **II** and **IV** are close to each other but may be differentiated by colour tests. The difference in distance of migration is greatest at pH 4·0. The spots are most satisfactorily revealed by successive spraying with sodium nitroprusside (1%), hydroxylamine hydrochloride

(1%) and *N* NaOH soln. The limit of detection is 5 to 10 μg. K. SAITO

671. **The non-aqueous titration of PAS [4-aminosalicylic acid], sodium PAS, and some commercial preparations.** L. G. Chatten (Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 556–558.—Rapid and accurate methods have been developed for the non-aqueous titration of 4-aminosalicylic acid (**I**) and its sodium salt (**II**) to visual end-points. The precision is good (coeff. of variation $\simeq 0{\cdot}2\%$) and the results compare well with those by the diazotisation procedure of the U.S.P. *Procedure*—For **I**, dissolve the sample (80 to 100 mg) in acetone (50 ml), add 0·5% thymol blue in anhyd. methanol (4 drops), protect the soln. from the atmosphere and titrate with 0·1 *N* KOH in anhyd. methanol to a blue end-point. For **II**, dissolve the sample (40 to 50 mg) in anhyd. methanol (50 ml), add thymol blue soln. (4 drops), protect from the atmosphere and titrate with 0·05 *N* $HClO_4$ in dioxan to a pink end-point. To assay samples of tablets of **I** or **II**, extract with solvent (40 ml), filter by suction through Whatman No. 1 paper, wash the funnel with solvent (10 ml) and titrate the combined filtrate and washings. A. R. ROGERS

672. **Application of micro-crystallographic methods to the detection of certain derivatives of nicotinic acid in medicinal preparations.** Z. Margasinski and H. Rafałowska (Zakład Chem. Inst. Leków, Warsaw). *Przem. Chem.*, 1955, **11**, 700–702.—A micro-crystallographic method based on the complex formation of the amide, diethylamide and hydroxymethylamide of nicotinic acid with certain compounds of copper, mercury and bismuth has been developed for their detection. The complexes have distinctive crystalline forms and are suitable for the differentiation of the above substances. The reagents used are $CuSO_4$ and NH_4SCN, Mayer's and Dragendorff's reagents. The crystals formed are illustrated. K. F. SPOREK

673. **Quantitative determination of leptazol by indirect complexiметric titration.** A. Paulsen (Univ. Farmas. Inst., Blinden, Oslo, Norway). *Medd. Norsk Farm., Selsk.*, 1956, **18** (8), 139–143.—*Procedure*—Dissolve leptazol (75 to 105 mg) in water (25 ml) and add slowly with stirring Cu_2Cl_2 soln. (B.P. 1953) (25 ml). Stopper the flask and set aside for 1 hr. in a refrigerator. Filter off the ppt. in a sintered-glass crucible IG3 and wash with 30 ml of water containing 1% (w/v) of glacial acetic acid. Transfer the crucible to a large beaker and add conc. HCl (5 ml) while stirring; then add water (30 ml) and continue stirring until the ppt. is completely dissolved. Add a few drops of 3% H_2O_2 and 10% aq. NH_3 until the soln. is alkaline and turns deep blue. After a few min. add 10% HCl until the soln. is just acid, when the colour changes to green. Next add *N* aq. NH_3 until the soln. is slightly alkaline and turns deep blue again. Add water up to $\prec$ 600 ml and 0·3 g of indicator (1% murexide in NaCl) and titrate at once with 0·1 *M* EDTA (disodium salt) until the colour changes to red - violet. One ml of 0·1 *M* EDTA (disodium salt) ≡ 0·007898 g of leptazol. P. HAAS

674. **The determination of 4-aminoquinoline antimalarials: revaluation of the induced fluorescence method, with specific application to hydroxychloroquine analysis.** E. W. McChesney, H. S. Wyzan and J. P. McAuliff (Sterling-Winthrop Res. Inst., Rensselaer, N.Y., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (9), 640–645.—The induced fluorescence method of Brodie *et al.* (*J. Biol. Chem.*, 1947, **168**, 319) for the determination of 4-aminoquinoline has been studied in detail with special reference to the determination of hydroxychloroquine in biological materials, and a specific procedure for the analysis of the latter is presented. Although it was not found possible to increase the precision originally claimed, the method has been considerably shortened and simplified by a number of modifications. K. A. PROCTOR

675. **Determination of carbon disulphide in its piperazine compounds.** R. E. Booth and E. H. Jensen (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 535–538.—This rapid spectrophotometric assay for CS_2 in the complex with piperazine (Parvex) or alkylpiperazines is based on acid hydrolysis and extraction of the liberated CS_2 into $CHCl_3$. Results agree well with assays for N, S or piperazine, on the assumption that piperazine is the only impurity. Nine replicate assays on one sample showed a coeff. of variation of 0·8%. *Procedure*—Mix the sample (120 mg) with $CHCl_3$ (100 ml) in a 200-ml pressure bottle. Add 14 *N* H_2SO_4 (10 ml) and immediately close tightly. Shake for one min., heat at 70° for 10 min. and cool under the tap. Strain a little of the $CHCl_3$ layer through cotton into a 1-cm cell and measure the extinction at 319 mμ. $E^{1\%}_{1\,cm}$ for CS_2 = 11·1. A. R. ROGERS

676. **Polarography of the ethylidinium ion of N-ethyl-N-1-naphthylmethyl-2-chloroethylamine [N-2-chloroethyl-N-etnyl-1-naphthylmethylamine].** N. G. Lordi and J. E. Christian (Sch. of Pharm., Purdue Univ., Lafayette, Ind., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (8), 530–531.—The polarographic reduction of the ethylidinium ion $R{\cdot}R'{\cdot}N{\cdot}CH_2{\cdot}CH_2^+$ (**I**) of N-2-chloroethyl-N-ethyl-1-naphthylmethylamine, of the thiosulphate ion, and of the reaction product $R{\cdot}R'{\cdot}N{\cdot}CH_2{\cdot}CH_2{\cdot}S_2O_3^-$ (**II**) of **I** with thiosulphate have been studied at various pH values. The reduction of both **I** and **II** is irreversible; the diffusion currents and $E_{\frac{1}{2}}$ values vary with pH. Gelatin (0·01%) was used as a maximum suppressor with **II** at a pH of 7. **I** decomposes slowly in soln.; **II** is stable. It is suggested that polarography is a suitable method of directly determining **I** in soln. A. R. ROGERS

677. **The volumetric determination of stilboestrol and stilboestrol dipropionate (Syntestrin).** I. Gyenes (Pharm. Factory of Kőbánya, Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 242–244.—Stilboestrol is determined essentially by the method of Sondern and Burson (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 358), except that the bromination is allowed to proceed for only 25 min. The probable limit of error is ± 0·3%. Alternatively, prepare an acetone - pyridine - methanol mixture (70:30:2), to each 100 ml add 0·1% azo violet in chlorobenzene (1 ml) and neutralise to blue - violet with 0·1 *N* K methoxide (**I**). Dissolve 100 to 125 mg of **I** in 50 ml of this solvent and titrate samples of 10 to 20 ml with 0·1 *N* **I**. The titrating soln. is standardised against cinchophen. The probable limit of error is ± 0·5%. To determine stilboestrol dipropionate (**II**), dissolve 72 to 82 mg in acetic acid (20 ml) in a 200-ml brominating flask. Add 0·1 *N* $KBrO_3$ (10 ml), H_2SO_4 (1:1) (0·5 ml) and KBr (300 mg in

1 ml of H_2O). Lubricate the joint with syrupy H_3PO_4 and keep the flask at 25° ± 3° for 80 to 83 min., protected from light. Add KI (500 mg) in H_2O (20 ml), followed by starch soln., and titrate with 0·1 *N* thiosulphate. A blank is carried out similarly. If the excess of Br is < 30%, the result is high; the time of bromination also affects the result. One mol. of **II** consumes 4 equiv. of Br. The probable limit of error is ± 0·5%.
A. G. PETO

678. **Polarographic studies of pharmaceuticals. I. Polarography of naphthaquinone derivatives.** Yutaka Asahi (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1956, **76** (4), 365–369.—Polarographic reduction waves of five naphthaquinone derivatives, Na 2-methyl-1:4-naphthaquinone-3-sulphonate, menaphthone, phthiocol, 2:3-epoxy-2-methyl-1:4-naphthaquinone and menaphthone - $NaHSO_3$ (all having vitamin-K-like action) were studied at various pH values. The reduction potential increases in the order given, decreasing with increase in pH value. Their polarographic determination can be carried out in a phosphate buffer soln. of pH 4 to 7 in the absence of the other homologues. K. SAITO

679. **Studies on purity tests. XIII. Tests of the reagents suggested by E. H. Vogelenzang.** E. Krogh-Svendsen, J. Zimmermann and F. Reimers (Dalgas Boulevard Pharm., Copenhagen, Denmark). *Medd. Norsk Farm. Selsk.*, 1956, **18** (7), 113–120 (in English).—Studies of Vogelenzang's limit tests for impurities in drugs by the addition of ethanol-containing seeding reagents for the induction of pptn., show that a seeding reagent is unnecessary for K, since pptn. with sodium cobaltinitrite in ethanol-containing test soln. gives reproducible results; a seeding reagent is similarly unnecessary in most cases with sulphate, since pptn. with *M* $BaCl_2$ gives reproducible results. When a seeding reagent is used, it should be freshly prepared for each test. O. M. WHITTON

See also Abstract 704.

Food

680. **Methods of determining the sugar content of sugar beets.** L. Westesson. *Socker Handl. I*, 1956, **12** (2), 7–13, and (in English) *Socker Handl. II*, 1956, **12** (2), 7–14.—The Schleiber, Soxhlet - Müller and digestion methods are discussed. A new extraction apparatus comprises three glass tubes inside one another. The outer tube is fitted with an evacuated double jacket and leads into the extraction flask. The middle tube has a glass bottom supported by a strip of rubber cloth in the exterior tube. The inner tube, in which the beet mush is placed, is open at both ends with a wire strainer-cloth wrapped round the bottom. Condensate from a copper spiral condenser drops on the mush. The extract passes through, rises to the rim of the middle tube and then flows down into a conical metal flask with a convex bottom. The test is made by mixing the homogeneous beet mush with lead acetate soln., boiling water and NaOH soln. (pH 7·5 to 8·0) and heating at 80° for 20 min. The mixture is then completely extracted (about 2 hr.) at 72° to 74° at 55 mm Hg, and the polarisation is measured on the cooled extract. A table is given showing a comparison of results obtained by this method, by a similar method using ethanol extraction and by the water digestion method. The mean difference between the water and ethanol extraction methods was constant at + 0·08 to + 0·09, whilst the water extraction and digestion method variation ranged from 0·00 to + 0·22, apparently because the digestion method is dependent on the marc content of the beet.
SUGAR IND. ABSTR.

681. **Colorimetric determination of betaine in glutamate process end-liquor [from sugar beet].** R. L. Focht, F. H. Schmidt and B. B. Dowling (International Minerals and Chem. Corp., Skokie, Ill., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (6), 546–548.—In the simple control method described, betaine is determined by measuring the colour of the reineckate ion in 70% acetone at 525 mμ, after betaine reineckate has been separated from an acid soln. of the sample. The betaine is determined by reference to standard curves. The pH of a soln. of 0·5 g of sample in 40 to 45 ml of water is adjusted to 1 with HCl. To this is added about 0·25 g of carbon and the soln. is heated nearly to boiling point. The hot soln. is filtered and the pH of filtrate and washings is again adjusted to 1 with HCl and the vol. adjusted to 100 ml. A 5-ml aliquot of this is cooled in ice, and 5 ml of aq. ammonium reineckate soln. [1·5% (w/v), pH 1] is added. After 3 hr. refrigeration, the betaine reineckate crystals are filtered off, washed with ether and dissolved in 25 ml of 70% acetone. The extinction of this soln. at 525 mμ is measured against an acetone blank. N. M. WALLER

682. **Rapid determination of calcium in sugar liquors.** J. R. Parrish (Rhodes Univ., Grahamstown, S. Africa). *S. African Sugar J.*, 1955, **39**, 543, 545.—Two methods are presented. Method (*i*) is recommended for molasses and juices that do not coagulate at the pH value used. Mixed juice is analysed by method (*ii*). *Method* (*i*)—Dilute 1·5 to 3·0 g of molasses with 25 to 50 ml of H_2O, add 5 ml of buffer (70 g of NH_4Cl, 600 ml of aq. NH_3, sp. gr. 0·9, made up to 1 litre) and transfer to an ion-exchange column (Zeokarb 226, 8 to 10 cm high, treated with dil. buffer). The flow rate should not exceed 10 ml per sq. cm per min. Wash the column with H_2O until the eluate is colourless. Elute with 60 ml of *N* HCl, followed by 40 ml of H_2O. Make the eluate alkaline with 15 ml of 6 *N* NaOH and titrate Ca^{2+} with 0·025 *M* EDTA (disodium salt), with murexide as indicator. *Method* (*ii*)—Add 1 g of Horne's basic Pb acetate to 100 ml of juice, stir, and dissolve 1 to 2 g of NaCl in the mixture; filter through rapid quant. paper, discarding the first few ml of filtrate. Take a 20-ml aliquot of filtrate, add five drops of dimercaprol soln. and 5 ml (or more) of 6 *N* NaOH (to dissolve the ppt.), then titrate Ca^{2+} with EDTA. If traces of Mn present in juices and molasses decolorise the murexide indicator, add hydroxylamine hydrochloride and more indicator.
CHEM. ABSTR.

683. **Quantitative determination of fibre present in tapioca starch and sago globules.** M. Narayana Rao, G. Rama Rao, M. Swaminathan and V. Subrahmanyan (Central Food Technol. Res. Inst., Mysore). *J. Sci. Ind. Res., B, India*, 1956, **15** (4), 202–204.—The presence of fibre to the extent of 1% in tapioca starch and sago globules is detected and approximately quantitatively estimated by a colorimetric method based on the aniline acetate colour test for pentosans. To the material under test (5 g) is added 10 ml of 13% HCl, followed by

10 ml of xylene. The mixture is heated in a boiling-water bath for exactly 10 min., cooled rapidly under tap water, shaken vigorously for 3 min. and centrifuged. The xylene layer is separated and dried with 1 g of anhydrous Na_2SO_4. A 2-ml portion of the xylene layer is added to a dry test-tube, 3 ml of aniline acetate reagent is added, the mixture is shaken and kept in the dark for 10 min. The intensity of the colour developed is measured with a Lovibond tintometer, with a 1-cm cell, or in a Klett - Summerson photo-electric colorimeter, with filter No. 52. I. JONES

684. **A viscometric micro-method for determining the α-amylase content of cereals and milling products.** B. Belderok (Centr. Inst. for Invest. of Foodstuffs, Wageningen, Holland). *Chem. Weekbl.*, 1956, **52** (35), 649–654.—A greatly increased content of α-amylase arises in wheat grains that have sprouted prematurely. A method is described for determining the percentage of wheat grains in a given sample which are thus affected. Use is made of a modified Zeitfuchs "cross arm" capillary viscometer (Johnson *et al.*, *Anal. Chem.*, 1952, **24**, 1505, and Miranda, *Chem. Weekbl.*, 1954, **50**, 741). Determinations are carried out on extracts made from 1 g of flour, after grinding with sand, but can also be carried out on as little as a single grain of wheat. As the presence of β-amylase reduces the viscosity of starch paste, a soln. of solubilised starch, previously treated with an excess of β-amylase, is used as a substrate; in such a soln. all the starch has been converted into erythrodextrin. Duplicate determinations should not differ by more than 0·02 or 0·03 Hoskam unit. A standard curve for determining the α-amylase content in Hoskam units is provided, together with numerical data comparing results obtained by this method with those obtained by using Hoskam's colorimetric method. For normal wheat the α-amylase content per grain is always $< 0{\cdot}5$ Hoskam unit. P. HAAS

685. **The determination of non-fat dry milk solids in bread by paper chromatography.** H. Zentner (Bread Res. Inst. of Australia, 111, Pacific Highway, North Sydney, N.S.W.). *Analyst*, 1956, **81**, 483–486.—In the method described, the air-dried sample is treated with ether to remove fat and is then extracted with 80% (v/v) ethanol under reflux. After removal of almost all the ethanol under reduced pressure the residue is diluted with water to a known vol. and pptd. protein matter is allowed to settle. The supernatant liquid (2 ml) is applied to filter-paper together with the same amounts of standard lactose solutions. The chromatogram is developed with a *n*-butanol - pyridine - water mixture containing $AgNO_3$ for 48 hr. The dried paper is exposed to NH_3 vapour for 1 hr., heated at $80° \pm 1°$ for 20 min., rinsed with $Na_2S_2O_3$ soln., washed in water and dried. The chromatogram is cut into strips and the densities of the silver spots are measured in a densitometer. The method eliminates the blank determination which is a source of error in fermentation methods. A. O. JONES

686. **A rapid method for the determination of solids-not-fat in milk.** A. G. Leggatt, D. W. Dinsmore and W. H. Sproule (Ontario Agric. Coll., Guelph, Ont., Canada). *Can. Dairy Ice Cream J.*, 1955, **34** (6), 50.—Fresh milk resists changes to its oxidation - reduction potential and the amount of this resistance has been found to be proportional to the solids-not-fat content. Titration with ceric sulphate accordingly is used to measure the solids-not-fat content of the milk. CHEM. ABSTR.

687. **A rapid method for estimating total protein in milk.** D. C. Udy (Agric. Res. Service, U.S. Dept. Agric., Washington, D.C.). *Nature*, 1956, **178**, 314–315.—Proteins will react quant. with anionic dyes to form insol. complexes (Fraenkel-Conrat and Cooper, *J. Biol. Chem.*, 1944, **154**, 239). A buffered soln. of Orange G is shaken with the milk sample and then centrifuged. The concn. of unbound dye is measured colorimetrically. The method is at least as accurate as, and quicker than, macro-Kjeldahl determinations. G. S. ROBERTS

688. **Application of the biuret reaction to the determination of the holoproteins in cows' milk.** M. Leclerc and A. Khodabandeh (Lab. de Chim. Biol., Fac. de Pharmacie, Paris). *Ann. Pharm. Franç.*, 1955, **13** (12), 749–752.—Various methods of separating the holoproteins from lactoserum are tested and thermocoagulation is selected as the most suitable. *Procedure*—Milk (1 ml) is diluted with 4 ml of water and 3 ml of the dilution is treated with 0·15 ml of 1% acetic acid solution (to pH 4·6). The solution is centrifuged, and the casein, washed with alcohol and ether, is dissolved in *N* NaOH and made up to 5 ml. The lactoserum (2 ml) removed from the casein is added with stirring, dropwise, to 20 ml of alcohol and heated for 4 min. over boiling water, while covered with a funnel containing a small tube of ice-water. The coagulum is centrifuged hot, washed with alcohol and ether, and dissolved in *N* NaOH. To each dissolved coagulum is added 4 ml of Gornall's reagent [$CuSO_4.5H_2O$ (1·5 g), Na K tartrate (6 g), NaOH (30 g), KI (1 g) and water to 1 litre] and after 0·5 hr. at 20° to 25° any ppt. is centrifuged off and the solution measured colorimetrically against a blank. The values obtained of 30 g of casein and $\simeq$ 3 g of holoproteins per litre are within the normal range. E. J. H. BIRCH

689. **Factors influencing the polarimetric determination of lactose in concentrated whey products.** M. A. House (United Dairies Ltd., Wood Lane, London). *Analyst*, 1956, **81**, 486–491.—Low results obtained in the polarimetric method for the determination of lactose in commercial whey are shown to be caused by the presence of one or more laevorotatory polypeptides formed when acid whey is left in contact with rennet curd. The optimum conditions for the formation of these substances are incubation of rennet curd with 1·6% lactic acid at 39°. Two types of laevorotatory material are obtainable from curd; one is removed by zinc ferrocyanide precipitants but the other is not so removed and remains in the serum prepared for polarimetric examination. The non-coagulable laevorotatory matter is adsorbed by fuller's earth and when eluted with aq. NH_3 gives a product with a fairly constant ratio of nitrogen content to optical rotation. Chromatographic examination of the amino acids obtained by acid hydrolysis of the purified material indicated the presence of leucine, valine, proline, α-alanine, glutamic acid, aspartic acid, arginine and possibly lysine. A. O. JONES

690. **Comparison of methods for determining water-insoluble acids (WIA) in butter.** L. G. Ensminger (Food & Drug Admin., Dept. of Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.).

J. Ass. Off. Agric. Chem., 1956, **39** (3), 769–772.—Low values were obtained for water-insoluble acids determined by the Ensminger hot-water wash procedure (*Anal. Abstr.*, 1955, **2**, 1946) on a sample of butter made from heavily neutralised cream. The melted butter (20 g) and hot water (200 ml) are therefore treated with conc. HCl (2 ml), and shaken well (10 sec.); the aqueous layer is separated, and three treatments with hot water (each 200 ml) are followed by separations. The fat is dissolved in ether (30 ml), the water that separates is removed, and the ethereal solution with ether rinsings is titrated (phenolphthalein) with 0·05 *N* Na ethoxide. The results are in good agreement with those afforded by the official (A.O.A.C.) method.

A. A. ELDRIDGE

691. **Studies on *iso*oleic acids. III. Quantitative estimation of the *iso*oleic acids of hydrogenated fats.** M. R. Subbaram and A. P. Mahadevan (Nutrition Res. Lab., Coonoor, India). *J. Sci. Ind. Res., B, India*, 1956, **15** (4), 198–201.—The composition of the *iso*oleic acid fraction in hydrogenated fats is determined by partition chromatography of the fraction on a silica-gel column. I. JONES

692. **Detection of hydrogenated dolphin oil in butter by the Bezzi and Sacconi method for triacetin.** D. Ongaro (Bologna, Italy). *Boll. Lab. Chim. Provenciali, Bologna*, 1955, **6**, 4–7.—The method is based on a fractional distillation of the water-sol. volatile fatty acids identical to that for triacetin (*cf.* Bezzi and Sacconi, *Ann. Chim. Appl.*, 1935, **25**, 407). Melt 10 g of butter, filter, and saponify with 40 g of glycerol and 4 ml of 50% NaOH; cool to 90°, add 180 ml of H_2O and 100 ml of H_2SO_4 diluted as for the Reichert - Meissl value determination. Distil and collect four successive 55-ml fractions, each in exactly 10 min. Filter each of the fractions through an 8-cm filter-paper, titrate 50 ml with 0·1 *N* NaOH, and calculate for 55 ml. The sum of the four titration values so obtained is multiplied by the following fractional coeff.—(*i*) 0·373, (*ii*) 0·285, (*iii*) 0·205, (*iv*) 0·138. There are thus obtained two values for each fraction, one experimental and one calculated. For genuine butter, the calculated and titration values are the same or nearly so. In mixtures of butter with hydrogenated dolphin oil, the algebraic sum of the differences between the titrated and calculated values for the first two fractions is positive; that for the last two fractions is negative, increasing with amounts of hydrogenated dolphin oil, from 10% to 40%, from 0·9 to + 3·2, and from − 0·9 to − 3·2, respectively. CHEM. ABSTR.

693. **A rapid method for the determination of total solids in tomatoes.** A. F. Mabrouk, A. A. Hussein and H. Aref (Dept. of Agric. Ind., Cairo Univ., Giza). *J. Sci. Food Agric.*, 1956, **7**, 257–261.—Experiments with a representative number of samples of tomatoes of Egyptian origin showed that the relationship between the total solids, by vacuum drying, and the refractive index of the raw pulp was linear, and that the solids could be calculated from the formula—total solids = $522{\cdot}60\ n_D^{20} - 695{\cdot}26$. The formula of Cruess was not applicable with accuracy since the equation used depends on the ratio of soluble to insoluble solids in the sample. D. G. FORBES

694. **Improved apparatus and method for the determination of the volatile oil content of spices.** L. A. Lee and C. L. Ogg (E. Regional Res. Lab., U.S. Dept. Agric., Philadelphia, Pa., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 806–816.—Modified apparatus for use in Clevenger's distillation procedure for determining volatile oil (*J. Amer. Pharm. Ass.*, 1928, **17**, 345) is described and illustrated. The rate of distillation is increased (3 to 4 ml of water per min.) by employing a magnetic stirrer, and the graduated portion of the trap is detachable. Values (v/w %) for volatile oil content thus obtained were—nutmeg 4·71, 4·76; 6·69 to 6·77; 4·89 to 5·09; fennel 1·48, 1·51; celery seed 2·62, 2·65; coriander 0·33, 0·34; cassia 2·28 to 2·31; 1·44, 1·46; mace 11·04 to 11·07; allspice 3·27 to 3·75; clove 16·38 to 16·51. A. A. ELDRIDGE

695. **Determination of original gravity of beer by means of the refractometer.** R. E. Essery (Brewing Ind. Res. Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 1956, **62** (2), 153–155.—The original gravity of beer can be calculated from equations derived from refractive index and present gravity values. This rapid refractometric method is less precise than the distillation method (standard deviation ± 0·747 as against ± 0·273); but is suitable for routine work. G. B. THACKRAY

696. **Spectrophotometric determination of dissolved oxygen [in beer].** H. van Cauwenberghe and J. de Clerck (Univ. Louvain, Belgium). *Bull. Ass. Anciens Étud. Brass. Louvain*, 1955, **51** (3), 97–109.—The colour reaction is based on the re-oxidation of reduced indigosulphonate soln. A sample is siphoned directly into a stoppered Coleman absorption cell, and 1 ml of a 1% soln. of indicator, previously reduced with sodium dithionite, is introduced by syringe, care being taken to avoid all contact with air. After 1 hr., the absorption is measured either at 600 mμ or at a lower wavelength if the oxygen content is too high. The reading is corrected for a blank and the oxygen content is determined from a calibration curve. The max. deviation is 5%. CHEM. ABSTR.

697. **Determination of mercury in beer.** A. M. Piette (Lab. Intercomm. Chim. et Bact., Brussels). *Ann. Falsif.*, 1955, **48**, 101–108.—Beer may contain Hg derived from proprietary "stabilisers." For the destruction of org. matter, the method of Andrews and Stringer (*Brit. Abstr. C*, 1952, 115) is followed with minor modifications, which include the use of hydroxylamine sulphate (not the hydrochloride) instead of $(NH_4)_2SO_4$ for the destruction of the nitrosyl hydrogen sulphate formed during the oxidation. The determination of Hg in the oxidation product is based on the use of the colour reaction with dithizone by (*a*) a visual comparative method (sensitive to < 60 μg of Hg per litre) in which Hg is separated from Cu, etc., by the method of Jacobs "Chemical Analysis of Foods and Food Products," 2nd Ed., 1951), or (*b*) the spectrophotometric method (sensitive to < 25 μg) of Irving *et al.* (*J. Chem. Soc.*, 1949, 151). In carrying out Jacobs' method, hydroxylamine sulphate is used instead of the hydrochloride for the destruction of excess of NO_2^-. The validity of both methods is confirmed.

P. S. ARUP

698. **New approach to the analysis of hop oil.** G. A. Howard (Brewing Ind. Res. Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 1956, **62** (2), 158–159.—Distillation and chromatographic methods of analysis of hop oil are discussed. Gas - liquid partition chromatography has separated 18 components of hop oil, of which myrcene,

methyl nonyl ketone, β- or γ-caryophyllene and humulene comprise more than 70%.

G. B. THACKRAY

699. **Determination of crude fibre in yeast.** F. Neumann (Zellstoff-Fabrik Waldhof, Mannheim, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 162–168.—After hydrolysis and washing, the residual fibre in yeast is best separated by centrifuging for 15 min. at 3000 r.p.m. Part of the fibre dissolves on being warmed and cannot therefore be indigestible cellulose. Moreover, the analytical results clearly indicate contents of heterogeneous material. The method adopted, results of which most closely approximate to results of animal-feeding experience, is that of Lepper (*Z. Tierernähr.*, 1940, **4**, 217).

J. P. STERN

700. **The determination of different forms of nicotinamide in wines.** J. Ribereau-Gayon, E. Peynaud and S. Lafourcade (20, Cours Pasteur, Bordeaux, France). *Bull. Soc. Chim. Biol.*, 1956, **38** (5–6), 923–930.—The use of three different micro-organisms showed the presence of five forms of nicotinamide activity in wines. Free nicotinamide (**I**) was determined directly with *Lactobacillus arabinosus* and total **I** by the same organism after alkaline hydrolysis in 3 *N* NaOH for 1 hr. at 120°. When *Kloeckera magna* was employed under the same conditions, higher results were obtained both before and after hydrolysis; two forms of activity not utilised by *Lb. arabinosus* but utilised by *K. magna* are therefore assumed to be present. The highest results were given by *Saccharomyces lactis β*, the concn. of activity being 5 to 10 times that given by *Lb. arabinosus*. The active substance determined by *S. lactis β* is destroyed by alkaline hydrolysis, is not trigonelline and does not appear to correspond with any known compound of the **I** class.

H. F. W. KIRKPATRICK

701. **Polarographic determination of malic acid in grape must and wine. II.** H. Grohmann and E. Gilbert (Weinabteilung Pfälz. Landw. VersSta. u. Chem. Untersuchungsanst., Speyer a. Rhein, Germany). *Z. LebensmittUntersuch.*, 1956, **103** (1), 32–41.—The method described is based on the quant. pptn. of the silver salt and the polarographic determination of malic acid in alcoholic soln. This pptn. of the silver salt enables the quant. separation of malic acid from lactic acid to be effected, and makes possible a simple determination of malic acid in dry and sweet wines, white wines containing a high content of lactic acid, dessert wines and must. In red wines and those of poorer quality derived from pressed grape skins, the interfering tannin present is first removed by treatment with ion exchangers before obtaining the silver ppt.

S.C.I. ABSTR.

702. **4-Hydroxybenzaldehyde-3-sulphonic acid as a reagent in the colorimetric fusel-oil determination [in spirits.]** A. P. Mathers and R. L. Schoeneman (Alcohol and Tobacco Tax Div. Lab., Int. Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 834–844.—Komarowsky's colorimetric method for the determination of fusel oil (*Chemikerztg*, 1903, **27**, 807, 1086) is modified by the use of Na 4-hydroxybenzaldehyde-3-sulphonate as the aromatic aldehyde. The sample of spirits (50 ml) is refluxed for 15 min. with 0·5 *N* NaOH (20 ml), and 50 ml of distillate is slowly collected. A mixture of 0·1 ml of distillate, 0·1 ml of reagent (1 g in 25 ml of water, filtered) and 2 ml of conc. H_2SO_4 is heated at 100° for 30 min.; after cooling it is diluted to 10 ml with conc. H_2SO_4 and the extinction is determined at 445 mμ. The extinction of an ethanol blank (0·1 ml of 50% ethanol similarly treated with the reagent) is deducted. A calibration curve is prepared with the aid of fusel-oil standards (0·1 ml) prepared from 1 ml of *iso*butyl alcohol and 4 ml of *iso*amyl alcohol diluted to 1 litre with 50% ethanol. Aliquots (0 to 50 ml) are diluted to 100 ml with 50% ethanol. For various whiskies and brandies the fusel-oil value (grams per 100 litres) determined by the Allen-Marquardt method (in which higher alcohols are lost during removal of the ethanol) was 65 to 70% of that determined by the modified Komarowsky procedure.

A. A. ELDRIDGE

703. **Determination of added distinctive cations in whisky. IV. Spectrophotometric determination of chromium, cobalt and manganese.** M. J. Pro and R. A. Nelson (Alcohol and Tobacco Tax Div. Lab., Int. Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 848–856.—For the determination of Cr the organic matter present in the whisky (10 ml) is destroyed with H_2SO_4 and HNO_3; the solution is diluted and neutralised, treated with $AgNO_3$ and $(NH_4)_2S_2O_8$ at controlled acidity, evaporated to half-volume, diluted, and treated with diphenylcarbazide solution. The extinction is determined at 546 mμ. Cobalt is determined in 20 ml of whisky by first destroying organic matter with H_2SO_4 and HNO_3, removing H_2SO_4 in a muffle-furnace at 500°, evaporating the residue with HNO_3, cooling, and then adding water, HCl and HNO_3, nitroso-R salt solution and Na acetate solution. The product is boiled, at first alone and then with HCl, and the extinction of the diluted solution is determined at 510 mμ. Manganese is converted into MnO_4^-; the whisky (25 ml) is evaporated to dryness, organic matter is burned off, and the residue is taken to fuming with H_2SO_4 and H_3PO_4. After dilution, HIO_4 is added; the solution is heated, cooled, and diluted, and its extinction is determined at 526 mμ. For 1 p.p.m. quantities the results are unaffected by the presence of any of 31 cations (1 to 10 p.p.m.) that may be added as markers.

A. A. ELDRIDGE

704. **Determination of quinine in quinquina aperitifs by paper chromatography.** J. Bonastre. *Ann. Falsif.*, 1955, **48**, 109–113.—The sample (25 to 50 ml) is mixed with *N* NaOH (2·5 to 5 ml) and continuously extracted with ether; aliquot portions of a soln. of the residue obtained after evaporation of the ethereal extract, in 2·5 ml of aq. 5% acetic acid, are used in parallel with aliquots of a 0·1% soln. of pure quinine in the same solvent, for quant. comparative chromatographic determinations, in which *n*-butanol containing 2% of aq. HCl (sp. gr. 1·18) and water to saturation (without excess) is used as ascending solvent on KCl-impregnated paper. Quinine is detected at R_F 0·95 by Munier's modified Dragendorff reagent, the composition of which is given. The method is sensitive to 1·5 to 2·5 μg of quinine with a quant. range of 2·5 to 20 μg; it is selective for quinine in the presence of the other cinchona alkaloids, for which reason the results obtained for aperitifs amount to ≃ 17% of the corresponding gravimetric results. Full working details are given.

P. S. ARUP

705. **Chromatographic identification of saccharin and dulcin in biscuits and chocolate.** M. Vietti-Michelina (Int. Merceologia, University, Turin). *Chim. e Ind.*, 1956, **38** (5), 392–393.—The two sweeteners are separated by chromatography from the alcoholic liquid resulting from the dialysis of the sample against ethanol at 95°. By chromatography on Whatman No. 1 paper, in a butanol-aq. NH_3 mixture, saccharin has an R_F of $\simeq$ 0·1, and dulcin has an R_F of $\simeq$ 0·8. By this method the separation and identification of 40 μg of saccharin and 200 μg of dulcin in a mixture can be effected. C. A. FINCH

706. **Recent advances in methods of analysis of oils and fats with special reference to micro-analytical procedures.** C. Whalley. *Paint Tech.*, 1955, **19**, 411–414; 1956, **20**, 7–10; 47–50; 85–90.—In this report of a series of post-graduate lectures, methods for the determination of physical constants (viscosity, refractive index, density, flash-point and molecular weight) are described, and recent procedures for the determination of chemical constants (acid value, sap. value, hydroxyl value, iodine value and peroxide value) are critically discussed. Microchemical methods for elementary and group analysis and for the determination of trace metals and of water are described, and include particulars of an apparatus for the rapid destruction of organic matter. The application of new analytical techniques, *viz*, ion exchange, paper chromatography and vapour-phase chromatography, to a variety of problems arising in oil and fat analysis is dealt with. D. R. DUNCAN

707. **Proposed revised official methods for the analysis of oils, fats and waxes.** D. Burton and G. F. Robertshaw (Leather Industries Dept., Leeds Univ., England). *J. Soc. Leath. Tr. Chem.*, 1956, **40** (5), 170–177.—Details are given for the proposed revised Official Methods of Analysis of the S.L.T.C. for sampling oils and fats, for separation of fatty matter from non-fatty matter, for determination of unsaponifiable matter (sterols, alcohols, and non-volatile mineral oil, etc.), and determination of saponification, acid, and iodine values. B. R. HAZEL

708. **Estimation of the safe dose.** J. H. Gaddum (Dept. of Pharmacol., Univ. of Edinburgh). *Brit. J. Pharmacol.*, 1956, **11** (2), 156–160.—Small quantities of toxic substances may be present in foods and it is sometimes necessary to decide what is the maximum quantity that can be regarded as safe. Statistical methods are described for obtaining from the result of a toxicity test a rough estimate of the largest dose which can be considered safe. G. F. SOMERS

See also Abstracts 542, 543, 549, 609.

Sanitation

709. **Iodimetric dead-stop determination of chlorine, and the colorimetry of chlorine in water chemistry.** J. Holluta and H. Meissner (Tech. Hochsch., Karlsruhe, Germany). *Z. anal. Chem.*, 1956, **152** (1–3), 112–133.—Some volumetric and colorimetric methods for the determination of free active Cl in water are compared for accuracy and it is shown that none is suitable as an absolute standard for low concn. of Cl (0·3 to 2 mg per litre). A dead-stop iodimetric method (*cf.* Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045) is developed which fills this need and permits 0·3 mg per litre of Cl to be determined with an accuracy within $\pm$1%. *Procedure*—First determine the blank of the apparatus by immersing the electrodes in very dil. H_2SO_4. Apply 200 mV and stir for 30 min., changing the medium several times. Then refill the cell with the sample (200 ml), 0·1 *N* H_2SO_4 (20 ml) and 2% KI soln. (10 ml). Read the galvanometer (the reading should decrease) and make sure this zero value is stable. Add previously standardised 0·001 *N* $Na_2S_2O_3$ (2 ml) and titrate with 0·001 *N* KIO_3 (added very slowly near the end-point). Generally three titrations are necessary for attaining a stable end-point. Solutions standardised by the dead-stop determination are used in an examination of two colorimetric methods for Cl, with *o*-tolidine (**I**) and *p*-phenylenediamine (**II**), respectively. The use of **II** in the usual manner gives low results on 0·3 mg of Cl per litre and these errors increase with increasing concn. of Cl. The use of **I** at pH 0·3 to 1·7 and of KF permits the determination of 0·25 to 1 mg of Cl per litre in the presence of 10 mg of Fe per litre with an accuracy within $\pm$ 1%. *Procedure*—Add 5% KF (1 ml) to the sample (70 ml) and then add the mixture to the soln. of **I** at 20°. Add conc. HCl (1 to 2 ml), mix, and determine the colour after 5 min. J. P. STERN

710. **Comparative fluoride analysis by several methods.** J. V. Thorn and G. P. Gribhob (Sanitation Lab., State Dept. of Public Health, Berkeley, Calif., U.S.A.). *J. Amer. Wat. Wks Ass.*, 1956, **48** (4), 455–461.—The principles of four published methods, *viz*, the standards method of the AWWA, the method of Megregian and Maier (M & M method), the method of Thrun (Eriochrome method) and the Rubin rapid method are described. These methods were used in a collaborative test (ten chemists). The standard deviation for each method was obtained by analysis of standard NaF solutions (0·3, 0·8 and 1·2 mg per litre) in the absence of interfering substances, and these deviations were applied to the mean values obtained for natural waters assuming that no interference occurred. The effects of interference are discussed; these differ according to the method used. The M & M method has a definite advantage, as a complete set of standards is not needed for each determination of F once the standard curve is constructed; however, interfering substances produce a much larger degree of error. Critical analysis of all the results leads to the conclusion that the M & M method and the Eriochrome method can be used in lieu of the standards method in works practice. The rapid method is not applicable at levels of F below 1 mg per litre, and is not reliable for water samples from many different sources. G. HELMS

711. **Improved sampling apparatus for water containing dissolved oxygen.** J. E. Houlihan and P. E. L. Farina (L.C.C. Southern Outfall Works, Crossness, Abbey Wood, London). *Analyst*, 1956, **81**, 377–379.—In taking pairs of identical samples of river water with conventional sampling apparatus, filling two bottles in series, the sample in the second bottle invariably showed 0·15 to 0·24 p.p.m. more dissolved O than the sample in the first. This was found to be due to water that had become aerated in the tubing running back into the sample. An improved sampling apparatus is described and illustrated. To prevent the return of water from the tubing into the sample, an enema-tubing valve

is inserted in the lower end of the outlet tubing. This, acting as a non-return valve, holds the column of water in the tube. In addition, the inlet tube is provided with stoppers or taps so that the samples are protected from atmospheric O during transit to the laboratory. A. O. JONES

712. **Determination of dissolved oxygen in waste water with a rotating platinum electrode.** Gô Okamoto, Takeshi Okura and Katsumi Goto (Faculty of Eng., Hokkaido Univ., Sapporo). *Japan Analyst*, 1956, **5** (7), 408–409.—Levine's polarographic determination of dissolved oxygen (*cf. Anal. Chem.*, 1954, **26**, 1297) was modified by the use of a rotating platinum electrode (600 r.p.m.). For the regulating soln., saturated KCl containing (hydrated) Na acetate (122 g) and glacial acetic acid (240 ml per litre) is recommended. The limiting current at −0·60 V is proportional to the concn. of dissolved oxygen (< 10 p.p.m.). No interference is caused by the presence of HNO_2. In the presence of a large amount of organic substance, the current is again measured subsequent to the removal of dissolved oxygen with N. The interference of atmospheric oxygen is also small (error < 5% for 2 p.p.m. of O) provided that the measurement is completed within 20 sec.

K. SAITO

713. **The possibility of the use of glass electrodes with a sodium function in water analysis.** P. A. Kryukov, M. M. Shul'ts and V. E. Goremȳkin. *Gidrokhim. Materialȳ*, 1955, **24**, 23–27; *Ref. Zhur., Khim.*, 1956, Abstr. No. 19,480.—The determination of the concn. of Na^+ with special glass electrodes is studied. It is established that glasses of a definite composition possess a strict sodium function not only in an alkaline but also in a moderately acid medium. Other cations in concn. exceeding the concn. of Na^+ up to a known limit do not influence the potential of the glass electrode. The anions Cl^-, SO_4^{2-} and OH^- do not exert a specific influence on the potential of the glass sodium electrode. The composition of glasses suitable for the preparation of electrodes with a sodium function is appended. The electrodes are calibrated with soln. of NaCl of known concn. Electrodes with a sodium function are more reproducible than those with a hydrogen function. The electrode potential does not change significantly with time. The diffusion potential is eliminated by using a saturated potassium chloride bridge. In most cases the error in the determination of the concn. of Na^+ does not exceed 7·1% as compared with the analytical determination. In only two cases did measurement with the electrode give results greatly different from the analytical results. These cases were characterised by a low concn. of Na^+ and a considerable excess of total Ca and Mg over the Na. In addition, one sample had a very low pH value.

C. D. KOPKIN

714. **Studies on mineral springs. II. Separation and determination of lithium ions.** Yasushi Mashiko and Yasuo Kanroji (Chem. Inst., Hot Spring Res. Centre, Kashiwagi, Shinjuku-ku, Tokyo). *J. Pharm. Soc. Japan*, 1956, **76** (4), 441–445.—The separation of Li and Na with a cation-exchange resin was studied for the purpose of the determination of Li in mineral springs (molar ratio of Li to Na, 1:1000). When a column of Amberlite IR-120 containing both ions is eluted with a mixture of 0·2 *N* HCl and methanol (1 + 1), all the Li (10 to 500 μg) is eluted in the 200 ml after the first 80 ml, whereas Na (< 230 mg) is not eluted in the first 350 ml. Lithium in the eluate is satisfactorily determined by the flame-photometric method at 670·8 mμ.

III. Determination of potassium ions. Yasushi Mashiko and Yasuo Kanroji. *Ibid.*, 1956, **76** (6), 689–693.—In the direct flame photometry of mineral water, the intensity of the K line at 768 mμ is greatly affected by PO_4^{3-}, SO_4^{2-} and Na^+ (< 500 p.p.m.). The salts, however, can be converted into chloride by passage through a column of Amberlite IRA-410 (Cl). The eluate is made up to 100 ml together with NaCl to make the sodium concn. 500 p.p.m. This soln. is submitted to flame photometry and the intensity of the K line is measured. No interference results from the presence of other metal ions in the mineral water. The working curve is linear for < 40 p.p.m. of K. K. SAITO

715. **Recommended methods for the analysis of trade effluents. Sampling and physical examination of the sample.** The Joint A.B.C.M. - S.A.C. Committee of Methods for the Analysis of Trade Effluents. *Analyst*, 1956, **81**, 492–498.—Recommended methods include methods for observations of colour and temperature and for determinations of pH values (by electrometric and colorimetric methods), transparency, solid matter settling in a definite time, suspended solids (by filtration or by centrifuging), total solids and dissolved solids. Recommendations for the sampling of certain types of effluent are given, and a simply constructed apparatus for the sampling of effluents containing immiscible liquids is described and illustrated.

A. O. JONES

716. **Estimation of diacetone alcohol in air.** R. S. Yunghans (Div. Ind. Hyg., Indiana Board of Health, Indianapolis, U.S.A.). *Arch. Ind. Hlth*, 1956, **13** (4), 336–339.—A rapid, simple method for estimating small amounts (≃ p.p.m.) of diacetone alcohol (**I**) in air is described. It is suitable for measuring the toxicity of air containing **I** and is developed from the Dal Nogare iodoform spectrophotometric method for estimating acetone and acetaldehyde in air (*Anal. Chem.*, 1951, **23**, 1473). The sample of air (1 to 20 litres) is drawn through water (10 ml) in a midget impinger, and 1 to 5 ml of the resulting sample soln. (containing ≯ 0·5 mg of **I**) is added immediately to a 125-ml separating funnel containing hypoiodite soln., made by adding 3·3 ml of a 20% aq. soln. of NaOH to 10 ml of iodine soln. [KI (400 g), I (200 g) and H_2O (800 ml)]. The funnel is stoppered immediately and the reaction is allowed to proceed for 5 min. If the orange - yellow colour is discharged, further iodine soln. must be added. After the reaction, the colour is discharged by adding two drops of 5% aq. $Na_2S_2O_3$ soln.; then 22 ml of $CHCl_3$ is added and the mixture is shaken well (150 times). The org. phase is transferred to a second 125-ml separating funnel containing 20 ml of H_2O and two drops of the $Na_2S_2O_3$ soln. and the mixture is shaken well (50 times). The org. phase is separated, filtered through No. 40 Whatman paper, and diluted to 25 ml with $CHCl_3$. The extinction of the diluted soln. is measured immediately in matched 1-cm silica cells at 347 mμ against $CHCl_3$ in a Beckman DU or similar spectrophotometer, with either a hydrogen discharge or tungsten light source. The amount of **I** is determined from calibration graphs prepared from standard soln. of **I**. Interference is caused by ethanol, acetaldehyde, methyl ketones and methyl carbinols that can be oxidised by hypoiodite to

methyl ketones; also by materials extracted with $CHCl_3$ which absorb in the wave band used. Freshly greased funnel-stoppers also upset the results and the grease must be removed with $CHCl_3$ before use. H. L. WHITEHEAD

See also Abstracts 358, 558, 581.

Agriculture and Plant Biochemistry

717. **Determination of partition coefficients of carotenoids as a tool in pigment analysis.** F. J. Petracek and L. Zechmeister (Calif. Inst. of Technol., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1484–1485.—A photometric method for the estimation of partition coefficients is described which facilitates the identification of carotenoid pigments. Results for the hexane - 85% methanol system are tabulated. E. G. CUMMINS

718. **Methods of chemical analysis of trace elements in biological materials. VIII. Analysis of plant ashes by polarographic method. 3. Use of cation-exchange resin.** Katsumi Yamamoto (Chem. Dept., Faculty of Sci., Tohoku Univ., Katabira-cho, Sendai). *Japan Analyst*, 1956, **5** (6) 340–342.—Trace amounts of Cu, Mn and Zn are eluted free from alkalis, SO_4^{2-} and PO_4^{3-} with 3 *N* HCl from a column of Amberlite IR-120, and polarographically determined in a soln. containing NH_4Cl and tartaric acid (*cf. Anal. Abstr.*, 1956, **3**, 2571). Plant ash is dissolved in *N* HCl and centrifuged, and the ppt. is treated with $(NH_4)HF_2$ and HCl and combined with the supernatant liquor. The soln. is adjusted to pH 2·0 and passed through the column, which is eluted first with 0·1 *N* HCl (to remove alkalis) and then with 3 *N* HCl. By the use of EDTA (disodium salt) instead of tartaric acid and NH_4Cl as supporting electrolyte (pH 6·2 to 6·4), only Cu gives a reduction wave.

K. SAITO

719. **Determination of phenolic groups in lignin preparations. Titration with potassium methoxide using dimethylformamide as a solvent.** J. P. Butler and T. P. Czepiel (Inst. of Paper Chem., Appleton, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1468–1472.—The method is based on the titration of a solution of the sample in dimethylformamide with K methoxide in benzene - methanol soln. The titration is followed potentiometrically with an Sb - calomel electrode system. By this method it is possible to differentiate between phenols (or enols) and more strongly acidic groups.

G. P. COOK

720. **Determination of total organic phosphorus in soils.** W. M. H. Saunders and E. G. Williams (Macaulay Inst. Soil Res., Aberdeen, Scotland). *J. Soil Sci.*, 1955, **6**, 254–267.—As part of a study of the distribution of P in a series of soil profiles from long-term field-experiment areas, total org. P was determined by a slight modification of the ignition - H_2SO_4 extraction method of Mattson *et al.*, and checked by the aq. NH_3 extraction method of Pearson. The results showed large discrepancies between these methods, and the effects of varying experimental conditions, as well as parallel tests with NaOH as the extracting agent, were investigated. Results obtained by extraction with hot 0·5 *N* aq. NH_3 were markedly dependent on acid pretreatment, the values being much lower than those obtained by the ignition method. Successive extractions with different concn. of aq. NH_3 and various temp. showed the main causes to be incomplete extraction and hydrolysis of org. P. Parallel tests showed that 0·1 *N* NaOH was much superior to 0·1 *N* aq. NH_3 as an extractant, cold extractions being preferable; values again depended on acid pretreatment. Values for organic P obtained by the ignition method were little affected by wide variations in ignition temp., acid concn., and period of extraction; double extraction with 2 *N* acid tended to give slightly higher values. Comparisons between the ignition method and a double extraction with cold 0·1 *N* NaOH following pretreatment with hot 0·1 *N* HCl showed that the values on the whole were very similar, with slightly higher ignition values. Although the NaOH values tended to be somewhat low owing to incomplete extraction and hydrolysis of org. P, the results could be regarded as minimum values. The ignition method was very simple and rapid, gave valid results, and was suitable for characterising soils in pedological studies and fertility investigations. CHEM. ABSTR.

721. **Rapid method for the determination of water-stable aggregates in soils.** W. T. H. Williamson, J. Pringle and J. R. H. Coutts (Dept. Soil Sci., Univ. Aberdeen). *J. Sci. Food Agric.*, 1956, **7** (4), 265–269.—Existing methods for the determination of water-stable aggregates in soil give variable results. Results reproducible within 1% can be obtained by drying the sample in a current of air at 35°, breaking large clods by hand and passing the soil through a 3-mm-aperture sieve. Up to 100 g (less for clay soils) of the sample passing the sieve is wetted by allowing it to stand overnight on a fine sieve with its base just immersed in water. The wet material is transferred to a bank of sieves (2-mm, 1-mm, 0·5-mm and 0·2-mm apertures) and mechanically agitated (10 min.) while a stream of water (1 gall. per min.) is passed through the apparatus. The material on the three larger sieves is dried at 105° and weighed. It is then puddled by rubbing down by hand on the 0·5-mm sieve under running water until the sand and gravel are clean, and the residue is re-dried and weighed. The difference in weighings is termed the true crumb structure of aggregates $> 0·5$ mm. The result given should be the mean of four determinations.

D. G. FORBES

722. **The identification and estimation of soil inositol phosphates.** G. Anderson (Macaulay Inst. for Soil Research, Aberdeen). *J. Sci. Food Agric.*, 1956, **7** (6), 437–443.—The soil, after acid leaching, is extracted with hot aqueous NaOH and, after successive pptn. to remove the bulk of the organic and inorganic concomitants, the phosphates are pptd. as the barium salts, which are converted into free acids and examined by one- or two-dimensional chromatography. The chromatograms are first developed with methanol - aq. NH_3 and after drying are developed at right angles with methanol - aq. NH_3 or acetone - acetic acid. Spots are located by the Wade and Morgan spray and their identity is checked against reference standards. About one-third of total soil organic phosphate consists of inositol hexaphosphate, the tetra- or tri-phosphate or their sum accounting for only 2 to 3%.

H. B. HEATH

723. **Determination of potassium as perchlorate in mixed fertilisers.** H. W. Berkhout (Agrik.-chem. Inst., Maastricht, Holland). *Z. anal. Chem.*, 1956, **152** (4), 248–253.—In the determination of K in

mixed fertilisers as $KClO_4$, NH_4^+ and SO_4^{2-} interfere and are removed by boiling with $Ca(OH)_2$ and subsequent addition of $BaCl_2$. Alternatively, SO_4^{2-} are separated from K^+ and NH_4^+ by a cation exchanger and NH_4^+ are removed from the eluted cations by $NaHCO_3$. The accuracy of the method is within ± 1%. Urea does not interfere. *Procedure*—Shake the sample (13·6 g) with water (450 ml) for 30 min., dilute to 500 ml, mix, and filter. Pass 25 ml of the filtrate through the cation-exchange column (granules of Imac C12). Wash the column with water (2 × 10 ml, 1 × 50 ml), reject the washings, and then elute with 4 *N* HCl (100 ml). Concentrate the eluate, treat the residue with a little water and 10% $NaHCO_3$ (10 ml) and warm for 5 min. Evaporate to dryness, cool, and then add water (10 ml), followed by 4 *N* HCl until dissolution is complete. Add $HClO_4$ (*d* 1·12; 15 ml), evaporate to dryness, and cool in a desiccator over H_2SO_4. To the dry mass add 0·3% ethanolic $HClO_4$ (10 ml), set aside, decant the liquid through a Gooch crucible, repeat the treatment thrice with ethanolic $HClO_4$ (⅄ 80 ml in all) and complete the filtration. Wash thrice with ethanol (20 ml in all), dry at 120° for 1 hr., cool in a desiccator over $CaCl_2$ or H_2SO_4, and weigh. J. P. STERN

724. **Flame-photometric determination of potassium in compound and mixed fertilisers.** Masakuni Shionoya and Chiaki Asano (Tokyo Fertiliser Inspection Office, 3–984, Nakameguro, Meguro-ku, Tokyo). *Japan Analyst*, 1956, **5** (7), 384–388.—The flame-photometric determination (with Lange's photometer) of K in various fertilisers was studied with reference to interference by acid radicals contained in their extracts. Water-sol. K in an ordinary compound fertiliser can be determined by the use of its aq. soln., the result being in good agreement with that by the conventional method. Since citric acid does not vitiate the estimation, it can be used to prevent the pptn. of $CaCO_3$. In the analysis of total K, a significant error results from the presence of an excess of HCl (0·2 mole per litre) but not from that of chloride. The results were statistically analysed and it was found that the flame-photometric method compares favourably with the gravimetric in respect of both accuracy and reproducibility. K. SAITO

725. **Some modifications in technique in the Perrin method for potash in fertilisers, including a mechanical shaker.** H. R. Allen (Kentucky Agric. Exp. Sta., Lexington, Ky., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 889–891.—In this modified Perrin method for determining K in fertilisers (*Ibid.*, 1953, **36**, 650), evaporation to complete the pptn. of K_2PtCl_6 is carried out in Erlenmeyer flasks containing weighed glass beads which are returned to the crucible with the ppt. The flasks are heated on a hot-plate equipped with a mechanical shaking device. A. A. ELDRIDGE

726. **Analysis for nitrogen in nitrate - chloride [fertiliser] mixtures.** O. W. Ford (Purdue Univ., Lafayette, Ind., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 763–765.—In the determination of N by the method described in "Official Methods of Analysis" (A.O.A.C.) 7th Ed., 1950, loss of N occurs when the ratio NO_3^-:Cl^- is 3:1 or less. The loss is prevented if the NO_3^- are reduced to NH_4^+ by means of reduced Fe and H_2SO_4 before digestion (*cf.* "Official Methods of Analysis," 1st Ed., 1920). A mixture of sample (0·5 to 2 g), reduced Fe (2 to 5 g) and water (25 ml) is treated after 15 to 30 min. with H_2SO_4 (1:1) (25 ml) and, after reaction has ceased, boiled for 15 to 20 min. If organic N is present, 50 ml of H_2SO_4 is used, and after being boiled the mixture is digested for 30 min. with 0·7 g of HgO. The product is cooled and diluted, K_2S and alkali are added, and the NH_3 is distilled off in the usual way. A. A. ELDRIDGE

727. **Photocolorimetric determination of phosphoric oxide in artificial fertilisers as the molybdovanadophosphate complex.** W. Kowalski and M. Szwanenfeld (Politechnika Śląska). *Przem. Chem.*, 1955, **11**, 698–700.—Existing methods for the determination of P_2O_5 are discussed. The gravimetric method, though accurate, was considered too long for plant control; the volumetric method was not accurate enough; the colorimetric method based on the formation of molybdenum blue was found to be sensitive to light and laborious. The colorimetric determination of the molybdovanadophosphate complex similar to that used for the determination of P_2O_5 in pig-iron and steel was found to be satisfactory. K. F. SPOREK

728. **A colorimetric determination of nitrofurazone in poultry feeds.** S. S. Thompson (J. Bibby and Sons Ltd., Gt. Howard St., Liverpool, England). *Analyst*, 1956, **81**, 443–444.—The method described for the determination of nitrofurazone (5-nitro-2-furfuraldehyde semicarbazone) added to poultry feeds in the prophylaxis of coccidiosis depends on the development of a pink colour when a 10% soln. of NaOH in 50% ethanol is added. The finely ground dried sample (5 g) is extracted with light petroleum and then with carbon tetrachloride by which all interfering matter is removed. The meal is then shaken occasionally during 1 hr. with 25 ml of dioxan, the extract is filtered, measured, diluted to twice its vol. with water, and the turbid liquid is filtered; 5 ml of the filtrate is treated with 1 ml of fresh 10% NaOH in 50% aq. ethanol. The transient colour is measured absorptiometrically without delay. The calibration graph is prepared with standard amounts of pure nitrofurazone in 50% dioxan. Concentrates (≃ 11%) may be extracted directly with dioxan. A. O. JONES

729. **Colorimetric method for determination of 4-hydroxy-3-nitrophenylarsonic acid in feeds.** J. W. Cavett (Dr. Salsbury's Lab., Charles City, Iowa, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 857–860.—The feed (5 g) is extracted with 2% $NaHCO_3$ solution (50 ml) and centrifuged; 30 ml is treated dropwise with HCl to precipitate the protein (pH 4 to 5). After centrifuging and decanting, the solution is brought to pH 12 with NaOH and treated with activated charcoal to remove yellow substances normally present in feeds and certain medicaments commonly added. The filtrate, and a sample of the filtrate treated with HCl, are then used for determination of the extinction at 410 mμ, the difference (read on a curve prepared from standards) representing the amount of 4-hydroxy-3-nitrophenylarsonic acid present. If water is used for the extraction and flocculation of the proteins is omitted, some feeds give high results. A. A. ELDRIDGE

730. **Determination of trace amounts of nicarbazin in chicken feed.** C. C. Porter (Merck Inst., Rahway, N.J., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 860–865.—The feed is extracted with ethyl acetate, which is removed at 50° to 80°, and the

residue is shaken with formamide and benzene. The benzene layer which separates on centrifuging is removed and the formamide solution is again extracted with benzene. After dilution with water, the formamide solution is shaken with a mixture of ethyl acetate and $CHCl_3$; the ethyl acetate - $CHCl_3$ layer is separated by centrifuging and washed with NaOH solution, and the solvent is evaporated from an aliquot. The residue is dissolved in ethanolic NaOH and the extinction at 426 mμ is determined before and after addition of acetic acid, the difference being compared with standards. Adherence to the quantities of solvents specified is important. The method is sensitive to $< 0{\cdot}0001\%$ of nicarbazin in feeds. The average recovery of added nicarbazin was 89·2%. Practically all of the usual macro-ingredients that yield coloured ethyl acetate extracts are removed by benzene, but furazolidone interferes. A. A. ELDRIDGE

731. **A new colorimetric method for pyrethrins.** H. L. Williams, W. E. Dale and J. P. Sweeney (Stored Products Insects Lab., U.S. Dept. Agric., Savannah, Ga., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 872–879.—The stored food-product is ground and extracted with Skellysolve F, and an aliquot of the extract is evaporated at 100°. The residue is treated with 5 ml of a mixture of 85% H_3PO_4 and ethyl acetate (4:1, v/v), shaken for 1 min., and heated at 100° for 3 min. After the red solution has been centrifuged and cooled, the extinction is determined at 550 mμ. Standards prepared from the sample with pyrethrin added in known quantity are used for comparison. A sample blank is subjected to the same procedure but without treatment with the reagent. Beer's law is obeyed for quantities up to 100 μg and as little as 7 μg can be accurately measured. Recoveries of added pyrethrins were 97 to 105%.
A. A. ELDRIDGE

732. **Determination of chlorine in hexachloro-*cyclo*hexane—Stepanow method.** E. Imerito. *Act. Bioquím., Santa Fé*, 1956, **5** (1), 23–25.—In a modification of the Stepanow method (*Ber.*, 1907, **394**, 4056; *J. Amer. Chem. Soc.*, 1909, **31**, 49), 0·4 g of hexachloro*cyclo*hexane is dissolved in 40 to 50 ml of butanol and the solution is made up to 100 ml in a calibrated flask with butanol washings from the solution flask. Of this, 25 ml is transferred to an Erlenmeyer flask fitted with a reflux condenser and boiled during the addition, over 40 min., of 2 g of Na. The solution is boiled for a further 30 min., then cooled to 50°, and distilled water (2 × 5 ml) is added via the condenser. The solution is neutralised with 3 *N* HNO_3 and 5 ml of 3 *N* HNO_3 is added to acidify. To the solution is added 25 ml of 0·1 *N* $AgNO_3$, followed by 3 ml of nitrobenzene and 2 ml of 15% ferric alum solution; the whole is agitated vigorously and the excess of $AgNO_3$ is determined with 0·05 *N* KSCN solution. A blank determination is also made and the chlorine content of the sample is calculated. The accuracy is of the order of ± 0·06%. D. LEIGHTON

733. **Measurement of chlorinated insecticide residues: a review of the methods.** S. V. Pingale and S. K. Majumder (Cen. Food Technol. Res. Inst., Mysore, India). *Bull. Central Food Technol. Res. Inst.*, 1956, **5** (9), 216–220.—Chemical, physical and biological methods are reviewed. The approach to the analysis of the residue, with particular reference to its detection and identification before the estimation, is indicated. (81 references.)
O. M. WHITTON

734. **Note on the detection of chlorinated organic pesticides in the paper chromatogram.** L. C. Mitchell (Food and Drug Admin., Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 891–892.—The developed chromatogram (*Ibid.*, 1952, **35**, 920; 1953, **36**, 553, 1183; 1954, **37**, 216, 530, 996; 1956, **39**, 484) is hung until apparently dry and then sprayed with a reagent prepared by dissolving 1·7 g of $AgNO_3$ in water, adding 10 ml of 2-phenoxyethanol and 50 ml of ethanol, and diluting with water to 200 ml. When apparently dry, the paper is exposed to ultra-violet light on both sides.
A. A. ELDRIDGE

735. **Determination of O-(3-chloro-4-nitrophenyl) OO-dimethyl phosphorothioate (chlorthion) residues in cottonseed.** M. J. Kolbezen and H. T. Reynolds (Univ. Calif., Citrus St., Riverside, Calif.). *J. Agric. Food Chem.*, 1956, **4** (6), 522–525.—The delinted, washed seeds are ground and extracted with light petroleum (boiling range 30° to 60°) and the extract, containing cottonseed oil and chlorthion, is subjected to partition extraction with light petroleum and methyl cyanide. Pigments and other interfering materials are removed from the methyl cyanide solution of chlorthion by chromatography through activated alumina. The chlorthion is extracted from the eluate with light petroleum, then reduced with Zn and H_3PO_4 before being treated with $NaNO_2$ solution, ammonium sulphamate and N-1-naphthylethylenediamine dihydrochloride solution to develop the colour. The extinction is measured at 545 mμ against a blank. The method is claimed to be sensitive to 0·02 p.p.m. of chlorthion in 200 g of cottonseed.
H. B. HEATH

736. **Colorimetric determination of the insecticide "Bayer 17147" (Gusathion).** O. Wollenberg (Bayer A.-G., Elberfeld, Germany). *Angew. Chem.*, 1956, **68** (17–18), 581.—The colour reaction for Gusathion (**I**) (the dimethylphosphorothiolothionic acid ester of N-methylbenzazimide) previously described (*cf. Anal. Abstr.*, 1956, **3**, 2575) has been made quant. *Procedure*—Mix a soln. of **I** (100 to 500 μg) in methanol (5 ml) with a 0·5% soln. of N-phenyl-1-naphthylamine in methanol (1 ml), H_2O (3 ml), 2 *N* $HClO_4$ (0·5 ml) and a 2% soln. of mercuric acetate in methanol (0·2 ml). Heat for 30 min. on a water bath at 50°, cool to room temp. and measure the extinction at 570 mμ. A. R. ROGERS

737. **The determination of 4-chloro-2-methylphenoxyacetic acid in MCPA by a differential refractometric method.** R. Hill (I.C.I. Ltd., Widnes, Lancs., England). *Analyst*, 1956, **81**, 323–329.—In the differential refractometric method described, the refractive index of a satd. soln. of pure 4-chloro-2-methylphenoxyacetic acid (**I**) is compared with that of a soln. of the sample so prepared that all the impurities are dissolved and the soln. is satd. with the main component. The difference in refractive index of the two soln. is an accurate measure of the impurities, provided that these are 4:6-dichloro-2-methyl- (**II**) or 6-chloro-2-methylphenoxyacetic acid (**III**) or both. The total MCPA is determined by extraction of the chloroformic soln. with $NaHCO_3$ soln., re-extraction from the

separated and acidified aq. layer with chloroform, and titration in ethanolic soln. with 0·1 *N* NaOH. The specimen for refractometry is prepared with ether as the extracting solvent, and this product serves also for determination of the equiv. wt. of the MCPA for the titration factor (*supra*). The extracted MCPA is dissolved in a mixture of *n*-butyl acetate and 2:2:4-trimethylpentane ("*iso*-octane") with enough pure **I** to ensure saturation. The differential refractometer is set with a soln. of the pure compound in the three cells and the contents of the middle cell are then replaced by the sample soln. and the difference in refractive index is measured. A calibration graph is prepared with artificial mixtures of **I** and the impurities (equal parts of **II** and **III**). A. O. JONES

738. **Infra-red determination of tetramethylthiuram disulphide in commercial dithiocarbamate formulations by the potassium bromide disc technique.** D. Firestone and P. J. Vollmer (Div. Food and Div. Cosmetics, Food and Drug Admin., Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 866–872.—Unlike dithiocarbamates, tetramethylthiuram disulphide exhibits a sharp absorption peak at 11·8 μ. The finely ground sample is mixed with powdered KBr and compressed to a disc which is used to obtain absorption curves from 6 to 15 μ. Standard discs are used to construct a curve, and corrections for interfering substances (methoxychlor and γ-hexachlorocyclohexane) are applied by absorption measurements at 11·8 μ and (for their determination) at the characteristic wavelengths of 12·6 and 12·9 μ, respectively.
A. A. ELDRIDGE

739. **Determination of mercury in fungicidal preparations containing organomercury compounds. I. The determination of organomercury compounds by direct titration.** K. F. Sporek (Plant Protection Ltd., Yalding, Kent, England). *Analyst*, 1956, **81**, 474–477.—Several analytical procedures for the determination of Hg in organomercury compounds are described. In the absence of halide ions many of these compounds can be titrated with standard NH_4SCN soln., with ferric alum as indicator, in the usual way. A list is given of a number of these compounds classified according to the sharpness of the end-point. The factor is double that used in inorganic titrations (1 ml of 0·1 *N* soln. ≡ 0·02006 g of Hg). A procedure by non-aqueous titration is described in which the compound is dissolved in a chloroform - propane-1:2-diol mixture and is titrated with standard HCl (9 ml of conc. HCl in a litre of the same solvent). The indicator is thymol blue. The compounds tested are tabulated with an indication of their behaviour with this procedure. A third method is based on a direct titration in aq. acetone with standard $HClO_4$ after liberation of the hydroxyl ion by treatment of the mercury compound with KI. Of the three methods described this is the only one applicable to the determination of organomercury chlorides.

II. The determination of organomercury compounds after decomposition to mercuric sulphide. K. F. Sporek. *Ibid.*, 1956, **81**, 478–482.—The method described depends on the formation of water-sol. complexes of certain organomercury compounds with Na_2S. The compound is extracted from the sample with conc. Na_2S soln. The extract is then boiled with dil. H_2SO_4 under reflux and the pptd. HgS is collected and oxidised; the mercury content is determined by titration with standard NH_4SCN, with ferric alum as indicator. Two procedures are described, one suitable for materials containing organomercury compounds in water-sol. diluents and the other suitable for materials containing diluents insol. in water and containing organic insecticides, dyes, pigments, etc.
A. O. JONES

See also Abstracts 539, 545, 548, 595, 609, 621.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

740. **Improvements in or relating to laboratory wash-bottle heads, splash heads or the like.** Quickfit and Quartz, Ltd., and D. Curtis. Brit. Pat. 755,966; Date appl. 20.11.53. The wash-bottle head comprises a conical ground-glass joint (for attachment to the flask) and a re-entrant dip tube extending axially through the joint cone and sealed by its upper end to the head above the joint. The conical joint has a skirt which extends below the ground portion and is furnished with three equally-spaced indentations to support the tube. J. M. JACOBS

741. **Cover glass for Erlenmeyer flasks.** F. R. Short and G. Good (Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1504.—The fabrication of a cover glass to fit Erlenmeyer flasks is described. The use of such a cover will enable very rapid evaporations to be carried out; the flasks may also be swirled or tipped to 45° without loss of the cover.
G. P. COOK

742. **Improvements in or relating to apparatus for aspirating predetermined volumes of gases.** L. Adams, Ltd. (Inventor: B. M. Wright). Brit. Pat. 756,186; Date appl. 20.1.54. Two plastic bottles, capacity ≃ 25 ml, are screwed into an aluminium alloy body provided with screw sockets for receiving them. A tap with a stainless-steel plug is formed in the body between the sockets and remains fixed when the bottles are rotated around it. Each bottle socket contains three passageways in one of which there is a stainless-steel air-inlet tube, in the second a stainless-steel jet, while in the third there is a plain hole. Bores are drilled in the plug of the tap so that the air-inlet tube in the upper bottle communicates with a suction nozzle and the plain hole associated with the lower bottle communicates with an outlet nozzle. In operation, water runs from the upper bottle through the plain hole and the bore in the plug to the lower jet which controls the rate of flow. Air is drawn into the upper bottle through the inlet nozzle while simultaneously air in the lower bottle escapes through the plain hole and the outlet nozzle. The apparatus aspirates at a rate varying from 7 ml per min., when full, to 6 ml per min. when nearly empty.
J. M. JACOBS

743. **Use of a wet gas meter in a sampling line operating under reduced pressure.** J. M. Horspool and R. F. Littlejohn (Brit. Coal Utilisation Res. Ass., Leatherhead, Surrey, England). *Chem. & Ind.*, 1956, (35), 915–916.—A wet gas meter is used for measuring the volume drawn through a sample train under reduced and varying pressure. The device is an adaptation of the principle of converting a filter pump into an air blower. Measurements

are accurate to within 0·1 litre for the lowest sampling rate (0·5 litre per min.) and within 0·2 litre for the highest (2·3 litres per min.). This error appears to be independent of the volume sampled.
O. M. WHITTON

744. **The analysis of gases at low pressures.** M. A. Cayless (British Thomson-Houston Co., Rugby, England). *Brit. J. Appl. Phys.*, 1956, **7** (1), 13–16.—The construction and operation of an all-glass apparatus for handling and analysing from 5 to 100 μl of gas at low pressure are described. Manipulation is entirely over mercury and the sample can be introduced into vacuum or discharge devices at pressures as low as 10^{-2} mm of mercury. Evolved gases can be identified and separated, at pressures between 10^{-3} and 1 mm of mercury, on the basis of measurements of v.p., diffusion and absorption. The error is $\simeq 2\%$ on samples of 5 to 100 μl. The technique is useful for studying the behaviour of cathodes in the presence of various gases and for the analysis of gases evolved from hot glasses or metals and electrodes under bombardment.
W. J. BAKER

745. **An ionometer for instantaneous determination of pH.** E. Dannenberg. *Act. Bioquim., Santa Fé*, 1956, **5** (1), 22–23.—The Gillespie method for determining pH, involving the preparation of series of dilutions of an alkali (0·1 *N* Na_2CO_3) and of an acid (partly neutralised acetic acid) of pH 4, is discussed. With indicator added to the dilutions, examination of the colour across a pair of complementary tubes of the same diameter gives the appearance of the indicator when added to a solution of pH equivalent to that obtained by mixing the solutions. A table is given of complementary dilutions corresponding to pH values at intervals of 0·1 between 6·0 and 7·8.
D. LEIGHTON

746. **A simple alternative to acetylated paper for use in chromatography.** P. Harris and F. W. Lindley (Courtaulds Ltd., Droylsden, Manchester, England). *Chem. & Ind.*, 1956, (35), 922–923.—With the chromatographic paper described and butyl acetate - pyridine - H_2O (1:5:10) as eluent, isomeric phenols, disperse dyes, and certain organic pigments have been separated successfully. A secondary cellulose acetate yarn is extracted with light petroleum (boiling range 40° to 60°), dried at 60°, and dissolved in dry acetone to give a 1% soln. The paper strip is immersed in this soln. for 15 min., drained, and dried quickly in warm air. The separation of the three isomeric toluidines by the use of this eluent (*cf.* Micheel and Schweppe, *Mikrochim. Acta*, 1954, 53) was not successful.
O. M. WHITTON

747. **Use of a large filter-paper sheet in circular paper chromatography by descending technique.** N. C. Ganguli (Univ. Coll. of Sci. and Technol., Calcutta, India). *Experientia*, 1956, **12** (1), 38–39.—A Whatman No. 1 filter-paper (50 cm × 32 cm) is cut 7 cm from the shorter side and parallel to it to form a 5-mm slit interrupted in the centre for 5 mm. The paper is spotted at this centre piece between the slits and when the paper is placed in solvent it will flow only through this constriction and radiate outwards to the main paper sheet, by the descending technique. About 50 μl containing 30 to 40 μg of individual amino-acids can be chromatographed. The solvent [*n*-butanol - acetic acid - water (4:1:1)] is added after a 24-hr. saturation period and the paper is developed by the descending technique. The solvent takes 24 hr. to travel a radial distance of 25 cm.
R. S. TONKS

748. **Elution apparatus for the quantitative evaluation of paper chromatograms.** R. Serzisko and M. Schieritz (Inst. Food Research, Potsdam-Rehbrucke). *Chem. Tech., Berlin*, 1956, **8** (4), 207–210.—The simple elution apparatus described enables a rapid and simultaneous elution of a number of chromatographic filter-paper strips to be made. The strips hang down from troughs of the elution liquor (fed from a supply vessel) and pass down through slits in the troughs, the top end of each paper strip being supported by lapping round a glass rod, which acts as a seal to the slit. Unoccupied slits are sealed with empty rods. The apparatus enables up to 16 strips to be eluted simultaneously in minimum time, in about 15 to 75 min. according to the quality and absorptive properties of the filter-paper. Test determinations of glucose with the use of the apparatus (with water as elution liquid) give accurate results.
H. L. WHITEHEAD

749. **A constant-temperature chromatographic tank.** W. Ensslin (Inst. Angew. Bot., Univ., Tübingen, Germany). *Z. anal. Chem.*, 1956, **153** (1), 1–4.—A thermostatic tank for descending chromatography is described which has a temp. deviation of $\simeq \pm 0{\cdot}1°$ for temp. above room temp., and $\simeq \pm 0{\cdot}2°$ to 0·3° for temp. below room temp. The apparatus consists of a PVC tank surrounded by a water bath and covered by a felt hood. The water bath is warmed by an electrolytic heater containing saturated NaCl soln.
J. H. WATON

750. **Chromatographic analysis of gases and vapours.** C. Rouit. *Rev. Inst. Franç. Pétrole*, 1956, **11** (2), 213–230.—The techniques of gas chromatography are reviewed and the details (absorbent, temp., carrier gas, etc.) of the method as applied to various gases and vapours are tabulated.
S.C.I. ABSTR.

751. **Convenient alkoxyl apparatus.** H. G. Arlt, jun., and K. Sarkanen (State Univ. N.Y., Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1502.—A modified alkoxyl flask and vapour-bath heater having improved temp. control and greater compactness is described.
G. P. COOK

See also Abstract 341.

Optical

752. **A new spectroscope for visual analysis.** R. H. Tyas (B.I.S.R.A., Hoyle Street, Sheffield). *Metallurgia, Manchr*, 1956, **53**, 285–288.—The Fuess metal spectroscope embodies several features new to metal spectrographic analysis, including a compact high-dispersion optical system, two sample tables with guide rods to permit spectra to be examined simultaneously, a photometer attachment for intensity comparisons and a variable-current intermittent a.c. arc. With these refinements, rapid routine operational ability is quickly acquired, particularly in the comparison of known and unknown materials, and results of high precision (coeff. of variation $\pm$ 8% or better) can be obtained with little extra experience.
J. O. LAY

753. **Simple quantitative analysis of elements in solution by flame photometry.** Yasumitsu Uzumasa, Seiichiro Hikime and Hitoshi Yoshida (Chem. Dept.,

Faculty of Sci., Hokkaido Univ., Sapporo). *Japan Analyst*, 1956, **5** (6), 327–329.—Since the log. of the intensity of the Cd line 2265 A increases linearly within the range 0·01 to 10 g per litre, it was used as a universal internal standard for common elements, such as Fe (2395·6 A), Al (3961·5), Ca (3179·3), Mg (2852·1) and B (2497·7), with a modified atomiser (Uzumasa *et al.*, *J. Chem. Soc. Japan*, 1933, **54**, 632; 1934, **55**, 622; 1935, **56**, 1174) of the Lundegårdh type. Satisfactory working curves were obtained for Fe (20 to 200 p.p.m.), Al (8 to 300 p.p.m.), Ca (20 to 200 p.p.m.), Mg (1 to 100 p.p.m.) and B (5 to 100 p.p.m.). The relative error was $<10\%$ in their mixture (for B the error is slightly greater). K. SAITO

754. **The flame-photometric analysis of oxide-coated cathodes.** J. Ádám, K. [Mrs. L.] Ettre, G. Gergely and P. F. Váradi (Telecommun. Res. Inst., Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 223–225.—The coatings contain Ba, Ca and Sr. If the cathode is W, the oxides are dissolved off with HNO_3 (1:1); if it is Ni, the oxides are scraped off and then dissolved in HNO_3 (1:1) as Ni must be absent at this stage. The apparatus, method and evaluation have been described earlier (*cf. Anal. Abstr.*, 1956, **3**, 606); Ba is determined at 4934 A, Sr at 4607 A, and Ca at 4226 A. Results obtained on samples as small as 5×10^{-6} g were reproducible to within 2 to 3%. A. G. PETO

755. **Effect of phosphoric acid in flame-photometric analysis.** Syoji Tsuchihashi and Eiichi Sekido (Faculty of Sci., Kobe Univ., Higashinada-ku, Kobe). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 708–712.—The effect of H_3PO_4 on the intensity of Ca lines was studied with the oxy-hydrogen flame. The intensity decreases with increase in concn. of PO_4^{3-} and becomes const. when the molar ratio Ca:P reaches 2:1. This effect is independent of the pH, the viscosity and the formation of any complex compound having an absorption band in the visible and u.v. region. Since the relative intensity of Ca lines at 662 mμ (CaO band), 554 mμ (CaO) and 422 mμ (Ca resonance line) remains const. irrespective of the concn. of PO_4^{3-}, the formation of a phosphate complex of Ca appears to take place in the flame. K. SAITO

756. **The spectrographic analysis of alpha-active materials by the copper spark method.** F. T. Birks (A.E.R.E., Harwell, Berks., England). *Spectrochim. Acta*, 1956, **8** (3), 167–179.—The spectrographic analysis of alpha-active materials using the reproducible and highly sensitive copper spark method of Fred *et al.* (*J. Opt. Soc. Amer.*, 1947, **37**, 279) is described. The active samples are sparked on copper electrodes in disposable plastic cassettes which are enclosed in a secondary chamber. The excitation source is a 30-kV high-wattage Feussner-type generator with ^{204}Tl sources in place of the usual mercury lamp to ionise the synchronous interrupter gap. The spark source and spectrograph are housed in separate laboratories, the light from the source being transmitted through quartz windows and a lens and then reflected from a front surface mirror into a Hilger large quartz spectrograph. A brief description is given of the laboratory specially designed for this purpose. The internal standard is Mo, 4 μg of which is dried on to the electrode by infra-red heaters. The preparation of standards and working dilutions is described and the line ratios and working curves for 14 elements as well as the detection sensitivities of 38 impurity elements are given. The coefficient of variation of the estimations is from 5 to 10% at the 5-μg level. K. A. PROCTOR

757. **Spectrochemical analysis with the help of time-resolved spark spectra.** Á. Bardócz and F. Varsányi (Spectroscopic Dept., Central Physical Res. Inst., Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 245–246.—The continuous background of spark spectra and the spectrum of the material of the electrode was separated by means of an optical system containing a rotating mirror and an electronically controlled high-tension spark source. Thus the interference due to the background is eliminated and the sensitivity is increased. A. G. PETO

758. **An attachment for the measurement of the absorption spectra on paper chromatograms.** C. Eger (Sci. Dept., Min. of Defence, Tel-Aviv, Israel). *Experientia*, 1956, **12** (1), 37–38.—The attachment consists of a rectangular brass box housing a circular paper-strip holder for the chromatogram and for blank paper. The papers pass two windows in the box which are brought into the light path of a Beckman DU quartz spectrophotometer successively by replacing the cuvette with the box between the photo-tube and monochromator. Scanning is carried out at several wavelengths in succession, measurements being made every 5 min. R_F values are determined at the wavelength of max. absorption of the substance. Transmission of dense chromatograms can be increased by immersing the paper strip in liquid paraffin. R. S. TONKS

759. **A note on the ultra-violet absorbance of aqueous paper-filtered filtrates.** D. J. Miller (Food and Drug Admin., Dept. of Health, Educ. and Welfare, Buffalo, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (3), 892–893.—Even in the absence of visible fibres or suspended material, an appreciable error in extinction can be introduced in the lower ultra-violet range when aqueous solutions are filtered through paper. The effect appears to be due to soluble matter. A. A. ELDRIDGE

760. **Infra-red [absorption spectra] analysers.** E. V. Rouir (Lab. de Recherches Physiques des A.C.E.L., Charleroi, Belgium). *Ind. Chim. Belge*, 1956, **21** (3), 221–234.—The principles of i.r. absorption spectrometry are reviewed and applied to the basic conception of the non-dispersive i.r. analyser. Various designs and uses in this field, including apparatus with single beam, differential apparatus with internal or external filter (positive or negative), and recently developed triple-beam analysers, dispersive or with a selective modulator, are described. (19 references.) S.C.I. ABSTR.

761. **Modification of bolometer and bolometer circuits of an infra-red analyser.** A. W. Wotring, R. F. Wall and T. L. Zinn (Monsanto Chem. Co., Texas City, Texas, U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1396–1399.—Consideration of element heating due to bridge current and source radiation, and heat losses due to conduction, convection and radiation has inspired the circuit and construction improvements described and illustrated which together have increased the signal to noise ratio in the Baird-BJI negative-type process monitor analyser by a factor of approximately 10. The two elements of the bolometer are thermally matched

at assembly, specially mounted, and operated in an electrically balanced, shielded, bridge. The recorder is tuned to the same frequency as the bridge voltage supply (60 cycles). An isolation transformer is fitted to the amplifier input circuit, which is adjacent to the bolometer. E. G. CUMMINS

762. **Systematic approaches to continuous infra-red analyser sensitisation.** W. J. Baker (Monsanto Chem. Co., Texas City, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1391–1396.—A method of sensitising a negative non-dispersive-type infra-red analyser so that it will detect a specific gas in a mixture of similar infra-red-absorbing gases is described. This method should be applicable to the selective detector type of analyser. The choice of material for sample-cell windows—quartz for sensitisation for methane in the presence of HCN, lithium fluoride for an analyser sensitive to ethylene in methane, ethane, propane and propylene—is discussed, and the composition of the interference-cell filling in this second case is determined. The final cell-fillings used for the filter, compensator and interference cells are tabulated, the concn. of the gas in the compensator cell being logarithmically related to the response of the analyser to that gas. The effect of pressure broadening is considered. E. G. CUMMINS

763. **Automatic derivative spectrophotometric titrations.** H. V. Malmstadt and C. B. Roberts (Univ. of Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1408–1412.—Full details for the construction of the titration cell and spectrophotometer circuit for fully automatic spectrophotometric derivative titrations are described. The instrument relates vol. of titration to the third derivative of the photometer output. In the examples examined, a precision of $\pm 0{\cdot}1\%$ is claimed at titrations of 5 ml per min. D. A. PANTONY

764. **Improvements relating to refractometer [cells].** LKB-Produkter Fabriksaktiebolag. Brit. Pat. 756,626; Date appl. 12.7.54 (Sweden, 16.10.53).—A special, compound double-prismatic cell, which has a range of linear response covering practically any refractive index difference, has mutually parallel entrance and exit walls for the light and 5 partition walls between them, establishing 2 groups of 3 prismatic components arranged in series. The medium to be studied, which has a refractive index n $(1 + \delta)$, constitutes one group of components, which alternate with those of the other group constituted by the reference medium with a refractive index n. The middle wall is parallel with the entrance and exit walls; the first and fifth walls are mutually parallel and form a given angle with the outer walls. The second and fourth walls are also mutually parallel and form, with the middle wall, an angle equal in magnitude to that given angle, but of opposite sign. The reference medium may be solid prisms of some optical material or may be constituted by a suitable reference liquid enclosed between the transparent walls. J. M. JACOBS

765. **Index of refraction as supplement to X-ray analysis of solid solutions. Ternary solid solutions.** L. J. Wood and H. H. Paproth (Dept. of Chemistry, St. Louis Univ., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1427–1430.—Correlation of the unit cell contour lines derived from X-ray measurements and the constant refractive index contour lines enables the composition of the system RbCl + KBr $\rightleftharpoons$ RbBr + KCl to be determined uniquely for any set of given conditions. D. A. PANTONY

Thermal

766. **Two miniature electric heating devices.** J. T. Stock and M. A. Fill (Norwood Tech. Coll., London). *Lab. Practice*, 1956, **5** (9), 344–345.—One device described is used on a retort stand or rod-frame assembly. The metal top and bottom plates (3 in. × 2 in.) enclose two heating elements rated at 60 W and 25 W, respectively. These elements, ranged side by side in firm contact with the top plate, are separated by asbestos board. A knuckle joint allows the hot-plate to rise and fall about rivets. The wiring gives an immediate choice of a heating capacity of 25, 60 or 85 W. The other apparatus, a rising-pillar miniature heater, is suitable for general microchemical operations such as fractional distillation and refluxing, particularly when sensitive and stable heat control is required. Either a 25- or 60-W heating element may be used in the hot-plate (2·5 in. × 1·5 in.). O. M. WHITTON

767. **A new thermal technique: derivative thermogravimetry.** L. Erdey, F. Paulik and J. Paulik (Dept. of Gen. Chem., Tech. Univ., Budapest, Hungary). *Acta Chim. Acad. Sci., Hung.*, 1956, **10** (1–3), 61–97 (in German).—The voltage of the current induced in a fixed coil surrounding a permanent magnet suspended from the beam of a balance is proportional to the rate of change of weight. An aperiodic automatic thermobalance has been adapted in this way to plot derivative thermogravimetric curves simultaneously with thermogravimetric and differential thermogravimetric curves. As a rule, the sample ($\simeq$ 1 g) is heated at 10° per min. The thermal analysis of a large number of samples (including minerals, industrial and agricultural raw materials and analytical ppt.) shows that the derivative curve is qual. characteristic of the decomposition process of certain substances (*cf. Nature*, 1954, **174**, 885). A. R. ROGERS

768. **Recording differential thermogravimetric balances.** P. L. Waters (C.S.I.R.O., Chatswood, New South Wales, Australia). *Nature*, 1956, **178**, 324–326.—Two balances are described which record continuously the rate of wt. loss as a function of time or temp., as well as the cumulative wt. loss. In one type the beam is maintained in equilibrium by a torsion wire actuated by a servo-mechanism, in the other by the change of wt. of an electrode of a silver coulometer. A proportion of the controlling voltage, or current, is recorded as a measure of the differential wt. change. Electro-mechanical summation of this value gives the cumulative wt. change. The torsion-wire balance can record total wt. changes of up to 0·5 g at $\gtrsim$ 30 mg per min. with an accuracy within 1%. The differential wt. change may be determined to within 0·2 mg per min. G. S. ROBERTS

769. **Organic quantitative analysis. V. Automatic electric combustion furnace for carbon and hydrogen determination.** M. Večeřa and L. Synek (Res. Inst. of Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1955, **49** (12), 1891–1894.—A new type of automatic electric furnace

for the determination of carbon and hydrogen is described. Various improvements in the arrangement are advantageous, especially for routine analyses. The arrangement is illustrated. The method has been tested for 3 years. J. ZÝKA

Electrical

770. **The location and quantitative evaluation of visible and invisible chromatographic zones by the R. Rf. [rectified radio-frequency] impedance method.** G. G. Blake (Univ. Sydney, N.S.W., Australia). *Anal. Chim. Acta*, 1956, **15** (3), 232–236.—A description is given of the quant. application of the rectified radio-frequency method for the location of chromatographic zones (*cf. Anal. Abstr.*, 1956, **3**, 1956). The chromatogram is developed, dried and then passed across the electrode-gap of the R.Rf. zone localiser, the Rf. current of each zone varying with the impedance. The rectified current is continuously recorded, and the areas of the graphs of solute distribution *vs.* current are measured with a planimeter. These areas (for the same amount of solute) are independent of the shape of the graph. Colourless zones or spots can be located and their areas measured without the need for staining or other treatment. W. J. BAKER

771. **Evaluation of paper electrophoresis by reflectance measurements.** L. Strauch ("Boris Kidrič" Chem. Inst., Ljubljana, Jugoslavia). *Klin. Wochschr.*, 1956, **34** (33–34), 906–907.—When a double-beam recording reflectance densitometer was used for measuring the colour of the dyed paper strips after electrophoresis of serum proteins, differing intensities were observed in the upper and lower sides of the paper. An even distribution can be attained by employing a suitable method of cooling during the electrophoresis and by drying at room temp. before measurements are made. The paper strip is stretched between two water-cooled plates and after electrophoresis it is stained in a soln. of Amido black 10B in methanol - acetic acid. The excess of dye is washed out with 1% acetic acid and the paper is air-dried for 24 hr. H. F. W. KIRKPATRICK

772. **Rapid analytical electrophoresis employing a prismatic cell.** G. Kegeles (Clark Univ., Worcester, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (9), 1459–1463.—An optical arrangement for moving-boundary electrophoresis with a cell of prismatic cross-section is described and illustrated. When refractive index gradient *vs.* the refractive index increment is plotted, the results show the arrangement to be comparable to a Schlieren system. Component concn. can be read with an eyepiece replacing the screen during the course of the experiment. E. G. CUMMINS

773. **Polarography and electrical methods of analysis.** G. F. Reynolds (Royal Arsenal, Woolwich). *Research*, 1956, **9** (5), 170–183.—A review is given of the major polarographic techniques, commencing with an explanation of the basic theory and describing inorg. and org. analysis, the dropping-mercury electrode and its various modifications and substitutes, instrumentation for linear-sweep oscillographic, subtractive, derivative and square-wave techniques and polarography of flowing solutions. Other electrical methods of analysis are described, including amperometric titration, dead-stop end-point titration, coulometry, at both const. potential and const. current, and high-frequency methods. (93 references.) S.C.I. ABSTR.

774. **The production of derivative polarograms.** J. Paulik and J. Proszt (Tech. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62** (7), 220–223.—The current is passed through the primary coil of a transformer; the current induced in the secondary coil gives directly the derivative of the polarographic current. The curve, registered on a photographic cylinder in the usual way, closely follows the non-derivative polarographic curve. It is symmetrical for an ideal step and does not show the shift often found in the method in which a condenser is used. Details are given for the construction of the transformer. A. G. PETO

775. **The automatic measurement of the drop rate of the dropping-mercury electrode, and its analytical applications.** P. Corbusier and L. Gierst (Univ. of Brussels, Belgium). *Anal. Chim. Acta*, 1956, **15** (3), 254–261.—A photo-electrically controlled electronic chronometer for measuring the drop rate (t) of the dropping-mercury electrode to within $\pm$ 0·1% is described. Relations are quant. established between t, interfacial tension (σ) and the concn. (C) of surface-active agents in an electrically conductive soln., and the possibility of determining C by this method is examined. Provided that the standard polarographic capillary and a drop height of $\simeq$ 100 cm are used, the measured values of t enable C to be calculated with a max. error of $\simeq$ 5%. In practice, most of the measurements are made in conjunction with a calibration curve constructed previously; the concn. of the surface-active agent in the soln., *e.g.*, aq. 0·1 *M* K_2SO_4, *M* NaOH or 0·1 *M* Na_2SO_3, should be $\not< 10^{-7}$ *M*. The rather poor selectivity of the method can be improved by judicious selection of supporting electrolyte and polarisation voltage. W. J. BAKER

776. **Observations on high-frequency indication [titration].** M. Oosting (Anal. Inst. T.N.O. Rijswijk, Holland). *Chem. Weekbl.*, 1956, **52** (36), 665–670.—To cover the great variety of applications of high-frequency methods the author proposes the term "indication" for "titration" as used by American authors. The advantages and disadvantages of this method are discussed. The method has been used for direct titrations of Cl^-, SO_4^{2-}, K, Pb and NH_4^+ in the presence of boric acid and for titrations in non-aqueous media. Details are given for the construction of a high-frequency indicator with a frequency of about 70 Mc.; the construction is simple and does not require any special knowledge of electronics. By a slight extension the apparatus can be employed for potentiometric titrations. P. HAAS

777. **The effect of an auxiliary electrode in high-frequency titration. (Appearance of a minimum point on the response curve in the region of high concentration.)** Kunio Nakano (Dept. of Chem., Faculty of Sci., St. Paul Univ., Ikebukuro, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (4), 551–556.—In high-frequency titrations with a coil-type apparatus (Nakano *et al.*, *Anal. Chem.*, 1954, **26**, 636), the overall resistance of the tank circuit decreases in a region of high concn. because of the secondary current in the coil. When an auxiliary electrode, which facilitates the flow of the

secondary current owing to its high conductivity, is placed in the sample container, a marked minimum appears on the response diagram (the resistance of the tank circuit plotted against the log. of concn. of the soln.). The concn. at which the minimum is observed depends on the frequency. By carrying out the titration in this region, there is a considerable increase in sensitivity (10 to 100 times) for both pptn. and neutralisation titrations.

K. SAITO

778. **An accurate transitometer [for coulometric measurements.]** L. Gierst (Univ. of Brussels, Belgium). *Anal. Chim. Acta*, 1956, **15** (3), 262–270.—A completely automatic "transitometer" for measuring, to within $\simeq 0{\cdot}005\%$, the "transition time" (t) during coulometric determinations at constant current in unstirred soln. (*cf. Anal. Abstr.*, 1955, **2**, 1121) is described, together with the associated circuits. The instrument has a dropping-mercury electrode with controlled surface, the area of which is known to within 0·05%. The electrolysis current is controllable to within 0·1%, whilst the electrode potential and t are determinable to within $\pm$ 0·4 mV and $\pm$ 0·1 millisec., respectively. Electrolyte concn. both above and below 10^{-4} N can be determined by this procedure with a max. error of $\simeq 0{\cdot}2\%$.

W. J. BAKER

779. **Automatic neutralisation and determination of acid addition with electrolytically generated base.** Masaki Nakanishi (Dept. of Chem., Ochanomizu Univ., Tokyo, Japan). *Nat. Sci. Rep., Ochanomizu Univ.*, 1955, **6** (1), 103–109 (in English).—An arrangement is described for the immediate and automatic coulometric neutralisation of added acid in unbuffered solutions. Beside the generator electrodes from a constant-current source, there are, in the cell, electrodes from a pH meter whose output operates a trigger at a preset pH to stop the current and the timer. The device is tested by determination of standard acid added dropwise. Provided the acid is added at a rate of less than $1{\cdot}244 \times 10^{-5}$ equiv. per min. (20 mA) the pH is automatically maintained between 7·0 and 7·5.

E. J. H. BIRCH

780. **Coulometric titrations using a pulse technique.** M. A. V. Devanathan and Q. Fernando (Univ. of Ceylon, Colombo). *J. Sci. Instrum.*, 1956, **33** (8), 323.—A multi-vibrator circuit supplies constant pulses to the titration cell via a high-speed relay which operates a post-office counter. The end-point of the titration is indicated by a permanent deflection in a micro-ammeter in an auxiliary circuit.

G. SKIRROW

781. **Improvements relating to the analysis of gases.** Mond Nickel Co., Ltd. (Inventor: P. Hersch). Brit. Pat. 750,254; Date appl. 23.10.53. (Addn. to Brit. Pat. 707,323 dated 12.1.53).—The original patent described a galvanic cell for determining the quantity of O in a gas by absorption of O at the cathode to produce an electric current which is a function of the concn. of O in the gas. The time lag was considerable, a reading within 5% of the final reading being reached only after 10 to 15 min. This sluggish response was due to the excessive height to which part of the cathode projected from the pool of the electrolyte and the large vol. of the electrolyte. The electrolyte is now retained by capillary action in a porous carrier, *e.g.*, a sleeve of porous poly(vinyl chloride), interposed between, and in contact with, an openwork cathode and the anode, whereby the gas makes contact with a dry surface of the cathode and the electrolyte with an opposed wet surface and there is a substantial length of three-phase boundary. The gas is caused to flow over the silver-gauze cathode at a rate so low that the current output per unit of O in the gas is proportional to the rate of flow of the gas.

J. M. JACOBS

782. **Small general-purpose cycloidal-focusing mass spectrometer.** C. F. Robinson and L. G. Hall (Consolidated Electrodynamics Corp., Pasadena, California, U.S.A.). *Rev. Sci. Instrum.*, 1956, **27** (7), 504–508.—Details are given of a small mass-spectrometer having good mass-resolving power, sensitivity and analytical accuracy up to mass 150.

G. SKIRROW

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (wt. in wt.)	%(w/w)
per cent. (wt. in vol.)	%(w/v)
per cent. (vol. in vol.)	%(v/v)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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